ASSESSMENT OF HEAVY METAL DEPOSITION IN SURFACE WATER AND SEDIMENT IN BALOK AND TUNGGAK RIVER, KUANTAN,

MALAYSIA

LIZA EVIANTI TANJUNG

MASTER OF ENGINEERING (CIVIL ENGINEERING)

UNIVERSITI MALAYSIA PAHANG

ASSESSMENT OF HEAVY METAL DEPOSITION IN SURFACE WATER AND SEDIMENT IN BALOK AND TUNGGAK RIVER, KUANTAN, MALAYSIA

LIZA EVIANTI TANJUNG

Thesis submitted in fulfillment of the requirements for the award of the degree of Master of Engineering (Civil Engineering)

Faculty of Civil Engineering and Earth Resources

UNIVERSITI MALAYSIA PAHANG

MAY 2013

UNIVERSITI MALAYSIA PAHANG

Name	:	<u>LIZA EVIANTI 7</u>	<u>FANJUNG</u>	
Date of birth	:	15 FEBRUARY	<u>1985</u>	
Title	:	ASSESSMENTA	OF HEAVY METAL	DEPOSITION
		IN SURFACE W	ATER AND SEDIM	ENT IN BALOK
	/	AND TUNGGAL	RIVER, KUANTAN	, MALAYSIA
Academic Sessio	on :	2012/2013		
I declared that th	nis thesis	is classified as:		
	NTIAL	(Contains confide	ential information und	er the Official
		Secret Act 1972)	*	
	CTED	(Contains restrict	tion information as sp	ecified by the
		organization whe	ere research was done,	,*
OPEN AC	CESS	I agree that my t	hesis to be published	as online open
Lo almorale doo 4h		access (Full text)	fallama
1 acknowledge tr	at Univer	sity Malaysia Pana	ing reserve the right a	s follows:
2 The Library	of Univer	sity Malaysia Paha	ng has right to make c	onies for the
purpose of re	search on	ly.	ing hus right to make e	opies for the
3. The Library l	has the rig	ght to make copies	of the thesis for acade	mic exchange.
Certified by				
LIZA EVIANTI	TANJUN	G	DR. WAN FAIZAL	BIN WAN ISHAK
Passport Number	: U03186	2	IC Number:72031703	35339
Date:		*	Date:	

RESTRICTICTED, please attach with the letter from the organization with period and reasons for confidentiality or restriction.

SUPERVISOR DECLARATION

I hereby declare that I have checked this thesis and in my opinion, this thesis is adequate in term of scope and quality for the award of the degree of Master of Civil Engineering and Earth Resources Universiti Malaysia Pahang.

		1			
Signature	:				
Name of Suj	pervisor :	Dr. WA	AN FAIZAL bin W	AN ISHAK	
Position	:	Senior I	Lecturer of Faculty	Industry Science an	nd Technology,
		Univers	siti Malaysia Pahan	ıg	
Date	:				
			UME		
			V		

STUDENT DECLARATION

I hereby declare that the work in this thesis is my own except for quotation and summaries which have been duty acknowledged. The thesis has not been accepted for any degree and is not concurrently submitted for award of other degree.



In the name of ALLAH,

I humbly dedicate to.....

My beloved parent Rasyidin Tanjung Khairana

My beloved family Fradina Yuliani Tanjung Mira Rizky Septiana Tanjung Boy Andi Azhari Tanjung Alif Fatar Syah Tanjung



Thank you.....

ACKNOLEDGMENTS

I would like to take this precious moment to express my sincere appreciation and grateful appreciation to my supervisor, Dr. Wan Faizal bin Wan Ishak, Master for this support, advice and for his germinal ideas and mentorship in my research.

I am grateful to Faculty of Civil Engineering and Earth Resources, Universiti Malaysia Pahang for the supported my research and study.

I would like to thank all the member of Postgraduate and Technical Staff of Faculty of Civil Engineering and Earth Resources, Universiti Malaysia Pahang for their assistance and sharing of expertise to me.

Especially, I would also like to address my unlimited thanks to my parents Rasyidin Tanjung, Khairana, to my sisters and brothers Fradina Yuliani Tanjung, Mira Rizky Septiana Tanjung, Boy Andi Azhari Tanjung, and Alif Fathar Syah Tanjung, My friends in UMP madam Sri Murni Astuti, M.Eng, DR. Awalludin Risch, Makson Rivai M.Eng, Ade Chandra Iwansyah M.Eng, Nurul Hidayah Saiffuddin, Mohammad Hisyam Abdullah, Xiao Rain M.Eng, Mupit Datusahlan, Irma Nurfitri, Nor Hindrawati, Erna Wati Ibnu Hajar, for support, their patience, love and trust in during my study.

I would like to take this precious moment to express my sincere appreciation and grateful appreciation to my internal examiner, Dr. Edryana Binti Abdul Aziz, Master for this correction my final thesis, support and advice. Thank you so much Dr. Edryana Binti Abdul Aziz for your suggestion to improve quality of my thesis.

ABSTRACT

Heavy metals are chemical elements with a specific gravity that is at least five times the specific gravity of water. The specific gravity is a measure of density of a given amount of a solid substance when it is being compared to an equal amount of water. Heavy metals are closely connected with environmental deterioration and the quality of human life, and thus have aroused concern all over the world. Heavy metals may enter the human body through food, water, air, or absorption through the skin when they come in contact with humans in agriculture and in manufacturing, pharmaceutical, industrial, or residential settings. Metal toxicity unlike some organic substances, are not metabolically degradable and their accumulation in living tissues can cause death or serious health threats. However, heavy metals deposition in water and sediment in Balok and Tunggak River is not well documented, and scientific evidence is very limited. The research proposed to assessment of heavy metals deposition in water and sediment in Balok and Tunggak River, Kuantan, Malaysia. Samples were collected every month from November 2010 to November 2012 and analyses for the regional variability for the concentrations of Al, As, Cr, Cd, Ch, Fe, Mn, Ni, Pb and Zn were done using ICP-MS. Rotary milling in agate mortar and microwave digestion (MDG) procedure was performed for the dissolution of the sediment samples before the determination of heavy metals. The presence of heavy metal has proven to influence human activity, mainly from chemical industry, chipboard industry, domestic waste disposal, etc.; they deteriorate since water quality of Balok and Tunggak River. Pearson's correlation between elements in water and sediment showed weak correlation due to the changing of the river flow rate every ±six hours. Principal Component Analysis (PCA) and Enrichment Factor (EF) had proven that sources of a pollutant were dominated by anthropogenic activity (industry and domestic waste) more than natural activity. The Contamination factor (Cf) proved that water column in Balok River and Tunggak River have been contaminated by Al, Cr, Mn, Fe, Ni, Cu, Zn, As, Cd, and Pb, which are probably influenced by anthropogenic activity, contamination by sedimentation, and natural source. Therefore, heavy metal pollution monitoring in Balok River and Tunggak River are needed in order to provide baseline data, which can be used by local authorities for environmental management, especially to improve river watermquality.

ABSTRAK

Logam berat adalah bahan unsur-unsur kimia dengan graviti khusus yang sekurangkurangnya 5 kali graviti tentu air. Graviti tentu adalah ukuran jumlah ketumpatan amaun yang diberikan bahan pepejal apabila dibanding dengan jumlah air yang sama rata air. Logam berat adalah berkait rapat dengan kemerosotan alam sekitar dan kualiti kehidupan manusia, dan dengan itu telah membangkitkan kebimbangan di seluruh dunia. Logam berat boleh memasuki tubuh manusia melalui makanan, air, udara, atau penyerapan melalui kulit apabila mereka bersentuhan dengan manusia dalam sektor pertanian dan pembuatan, farmaseutikal, industri, atau kedudukan kediaman. Ketoksikan logam tidak seperti beberapa bahan-bahan organik, adalah tidak terurai dan pengumpulan ia dalam tisu hidup boleh menyebabkan ancaman kematian atau masalah kesihatan yang serius. Walau bagaimanapun, pemendapan logam berat di dalam air dan sedimen di Sungai Balok dan Tunggak tidak direkodkan dengan baik, dan bukti saintifik adalah sangat terhad. Penyelidikan yang dicadangkan penilaian pemendapan logam berat di atas air dan sedimen di Sungai Balok dan Tunggak, Kuantan, Malaysia. Sampel dikumpulkan setiap bulan dari November 2010 hingga November 2012 dan analisis untuk kebolehubahan serantau untuk kepekatan Al, As, Cr, Cd, Ch, Fe, Mn, Ni, Pb dan Zn dengan menggunakan ICP-MS. Pengilangan Rotary di dalam proses mortar batu akik dan gelombang mikro penghadaman (MDG) prosedur telah dilakukan untuk pembubaran sampel sedimen sebelum penentuan logam berat. Turut hadir logam berat telah terbukti boleh mempengaruhi aktiviti manusia, terutamanya dari industri kimia, industri papan chip, pelupusan sisa domestik, dan lain-lain, mereka memberi menurunkan kualiti air Sungai Balok dan Tunggak. Korelasi Pearson antara elementelement di dalam air dan sedimen menunjukkan korelasi yang lemah disebabkan oleh perubahan kadar aliran sungai setiap ±6 jam sekali. Analisis Komponen Utama (PCA) dan Faktor Pengayaan telah membuktikan bahawa sumber bahan pencemar telah dikuasai oleh aktiviti antropogenik (industri dan sisa domestik) lebih daripada aktiviti semulajadi. Faktor Geoaccumulation telah membuktikan bahawa lokasi pensampelan di Sungai Balok adalah dari kategori untuk tidak tercemar sangat pencemar manakala tapak pensampelan di Sungai Tunggak termasuk kategori yang tidak tercemar ke sederhana tercemar. Faktor pencemaran dan tahap pencemaran telah membuktikan bahawa turus air di Sungai Balok dan Tunggak Sungai telah tercemar dicemari oleh Al, Cr, Mn, Fe, Ni, Cu, Zn, As, Cd dan Pb yang mungkin dipengaruh oleh aktiviti antropogenik, pencemaran oleh pemendapan, dan sumber semula jadi. Oleh itu, pemantauan pencemaran logam berat di Sungai Balok dan Tunggak Sungai diperlukan untuk menyediakan data asas yang boleh digunakan oleh pihak berkuasa tempatan bagi pengurusan alam sekitar pencemaran alam sekitar terutama untuk memperbaiki kualiti air sungai

TABLE OF CONTENT

SUPERVISOR DECLARATION				
STU	DENT D	ECLARATION	V	
DED	ICATIO	N	vi	
ACK	NOWLE	DGEMENTS	vii	
ABS	TRACT		viii	
ABS	TRAK		ix	
TAB	LE OF C	CONTENT	Х	
LIST	r of tai	BLES	xiv	
LIST	r of fig	URES	xvi	
LIST	r of syn	ABOL/ ABBREVIATIONS	XXV	
CHA	PTER 1	INTRODUCTION		
1.1	Backgr	ound	1	
1.2	Probler	n Statement	2	
1.3	Objecti	ves of the Research	3	
CHA	PTER 2	LITERATURE REVIEW		
2.1	Heavy	Metal	4	
2.2	The Ch	aracteristic of Heavy Metal	5	
	2.2.1	Aluminum	5	
	2.2.2	Chromium	6	
	2.2.3	Mangan	8	
	2.2.4	Ferrum	9	
	2.2.5	Nickel	10	
	2.2.6	Copper	12	
	2.2.7	Zinc	13	
	2.2.8	Arsenic	14	
	2.2.9	Cadmium	15	
	2.2.10	Plumbum (Pb)	18	

2.3	Toxicity of Heavy Metal	19
2.4	The occurrence of heavy metal in surface water	21
2.5	The accumulated of heavy metal in surface sediment	24
2.6	Study Area	27
2.7	Multivariate Analysis	28

CHAPTER 3 MATERIALS AND METHODS

3.1	Introduction	40
3.2	Selection of Monitoring Stations	40
	3.2.1 Location of sampling station at Balok River	42
	3.2.2 Location of sampling station at Tunggak River	45
3.3	Materials	47
	3.3.1 Equipment and Instrument	47
	3.3.2 Reagent and Chemical	48
3.4	Methods	49
	3.4.1 Sampling frequency	49
	3.4.2 Parameter Measurement	50
	3.4.3 Preparation of Water samples	50
3.5	3.4.4 Preparation of Sediment samples Analysis of heavy metal by ICP-MS	51 52
	3.5.1 Sample Preparation for Mineral Analysis	52
	3.5.2 ICP-MS Operating Condition	53
3.6	Analysis Statistic	54

CHAPTER 4 RESULT AND DISCUSSION

4.1	Introd	uction	56
4.2	Water	Quality Parameters for Balok River	56
	4.2.1	Chemical Oxygent Demand	57
	4.2.2	Biological Oxygen Demand	58
	4.2.3	Dissolved Oxygen	59
	4.2.4	Ammoniac Nitrogent	60

	4.2.5 Suspended Solid	61
	4.2.6 pH	62
	4.2.7 Water Quality Index (WQI)	63
4.3	Heavy Metal concentrations in water and sediment	
	in Balok River	65
4.4	Heavy Metal concentrations in water and sediment	
	of three sampling stations of Balok River	77
4.5	Relationship element in Location 1	99
4.6	Relationship element in Location 2	103
4.7	Relationship element in Location 3	107
4.8	Principal Component Analysis (PCA) on sediment in location 1	111
4.9	Principal Component Analysis (PCA) on water in location 1	114
4.10	Principal Component Analysis (PCA) on sediment in location 2	116
4.11	Principal Component Analysis (PCA) on water in location 2	118
4.12	Principal Component Analysis (PCA) on sediment in location 3	120
4.13	Principal Component Analysis (PCA) on water in location 3	122
4.14	Quantification of stream sediments pollution Balok River	124
4.15	Water Quality Parameters Analysis for Tunggak River	131
4.16	Principal Component Analysis (PCA) on water in location 3	122
4.17	Heavy Metal concentrations in water and sediment	
	in Balok River	151
4.18	Relationship element in Location 1	174
4.19	Relationship element in Location 2	178
4.20	Relationship element in Location 3	180
4.21	Principal Component Analysis (PCA) on sediment in location 1	183
4.22	Principal Component Analysis (PCA) on water in location 1	186
4.23	Principal Component Analysis (PCA) on sediment in location 2	188
4.24	Principal Component Analysis (PCA) on water in location 2	190
4.25	Principal Component Analysis (PCA) on sediment in location 3	192
4.26	Principal Component Analysis (PCA) on water in location 3	194
4.27	Quantification of stream sediments pollution Tunggak River	124

CHAPTER 5 CONCLUSION AND RECOMMENDATION

5.1	Introduction	203
5.2	Conclusion	203
5.3	Recommendation	206
5.4	Future Research	206

REFERENCES

207



APPENDICES

APPENDIX	A-1.7	Гhe average o in sediment В	f heavy metals co alok River (ppm)	oncentrations of three sampling p	ooints	233
APPENDIX	A-2.	The average of Balok River	of heavy metals c (ppm) during No	oncentrations in sed vember 2010 until J	iment uly 2011	234
APPENDIX	A-3.	The average of Balok River	of heavy metals c (ppm) of three sa	oncentrations in wat ampling points	er	235
APPENDIX	A-4.	The average of Balok River	of heavy metals c (ppm) during No	oncentrations in wat vember 2010 until J	er uly 2011	236
APPENDIX	A-5.	ONE-WAY in sediment	ANOVA of heavy of three sampling	y metals concentrations Balok River	ons	239
APPENDIX	A-6.	ONE-WAY sediment Ba	ANOVA of heav lok River during	y metals concentration November 2010 unt	ons in il July 2011	240
APPENDIX	A-7.	ONE-WAY in water Bal	ANOVA of heav ok River for three	y metals concentrations and the sampling points	ons	241
APPENDIX	A-8.	ONE-WAY in water Balo	ANOVA of heav ok River during N	y metals concentrat lovember 2010 until	ions I July 2011	242
APPENDIX	A-9.	The average of three samp	of heavy metals o plings stations Tu	concentrations in sec nggak River	liment	243
APPENDIX	A-10.	The average Tunggak Riv	of heavy metals ver (ppm) during	concentrations in se November 2010 unt	diment il July 2011	244
APPENDIX	A-11.	The average Tunggak Riv	of heavy metals over (ppm) of three	concentrations in wa	ter	245
APPENDIX	A-12.	The average Tunggak Riv	of heavy metals over (ppm) during	concentrations in wa November 2010 unt	ter il July 2011	247
APPENDIX	A-13.	ONE-WAY in sediment	ANOVA of heavy of three sampling	y metals concentration Tunggak River	ons	249
APPENDIX	A-14.	ONE-WAY Tunggak Riv	ANOVA of heavy ver during Noven	y metals concentrations where the second sec	ons in sedime 2011	nt 250
APPENDIX	A-15.	ONE-WAY Tunggak Riv	ANOVA of heavy	y metals concentration	ons in water	251

APPENDIX A-16. ONE-WAY ANOVA of heavy metals concentrations in water Tunggak River during November 2010 until July 2011 252

APPENDIX A-17 INTERM NATIONAL WATER QUALITY STANDARDS FOR MALAYSIA (INWQS)

253



LIST OF TABLES

Tab	le No. Title	Page
2.1	Would avances shale concentrations (nom)	
2.1	world average shale concentrations (ppm)	25
2.2	By (Turekian and Wedeponi, 1961) of monitored elements	35 25
2.2	Classification of enrichment factor (Losca and Wiechuya, 2003)	35
2.3	Guidelines for drinking water quality	36
2.4	CF and PLI values with their pollution grade and intensitas	37
3.1	Sampling Location	41
3.2	List of parameters analysed	50
3.3	Operating conditions for ICP-MS	53
4.1	Result of six water quality parameters	57
4.2	Status of River Pollution on Water Quality Index (WQI)	
	and Sub Index for Balok River	64
4.3	Average of heavy metals in sediment for three samplings sites in	
	Balok River during November 2010, March 2011 and July 2011	75
4.4	Trend of heavy metals in sediment for three samplings sites in	
	Balok River during November 2010, March 2011 and July 2011	76
4.5	Average of heavy metals in water for three samplings sites in	
	Balok River during November 2010, March 2011 and July 2011	76
4.6	Average of heavy metals in water for three samplings sites in	
	Balok River during November 2010, March 2011 and July 2011	76
4.7	Correlation matrix of level of heavy metals	
	in sediment and water samples location 1 Balok River	100
4.8	Pairs of correlation element in sediment sample	101
4.9	Pairs of correlation element in water sample	101
4.10	Pearson's correlation element in water-sediment in location 1	102
4.11	Correlation matrix of level of heavy metals	
	in sediment and water samples location 2 Balok River	104
4.12	Pairs of correlation element in sediment sample	105
4.13	Pairs of correlation element in water sample	106

4.14	Pearsons' correlation of element in water-sediment location 2	107
4.15	Correlation matrix of level of heavy metals	
	in sediment and water samples location 3 Balok River	108
4.16	Pairs of correlation element in sediment sample	109
4.17	Pairs of correlation element in water sample	110
4.18	Pearsons' correlation of element in water-sediment location 3	111
4.19	Matrix of the principal component analysis loading of metals	
	and major elements of river sediments in location 1 Balok River	112
4.20	Matrix of the principal component analysis loading of metals	
	and major elements of river water in location 1 Balok River	114
4.21	Matrix of the principal component analysis loading of metals	
	and major elements of river sediment in location 2 Balok River	116
4.22	Matrix of the principal component analysis loading of metals	
	and major elements of river water in location 2 Balok River	118
4.23	Matrix of the principal component analysis loading of metals	
	and major elements of river sediment in location 3 Balok River	121
4.24	Matrix of the principal component analysis loading of metals	
	and major elements of river water in location 3 Balok River	122
4.25	Enrichment Factors for stream sediments of study area	124
4.26	Contamination Factor and Pollution Load Index	
	of stream sediment	126
4.27	Contamination Factor and Pollution Load Index of stream water	129
4.28	Result of six water quality parameters	131
4.29	Status of River Pollution on Water Quality Index (WQI)	
	and Sub Index for Balok River	138
4.30	Trend of heavy metals in water for three samplings sites in	
	Tunggal River during November 2010, March 2011 and July 2011	149
4.31	Average of heavy metals in sediment for three samplings sites	
	in Tunggak River during November 2010, March 2011 and July 2011	149
4.32	Trend of heavy metals in water for three samplings sites	
	in Tunggak River during November 2010, March 2011 and July 2011	150
4.33	Average of heavy metals in sediment for three samplings sites in	
	Tunggak River during November 2010, March 2011 and July 2011	150

4.34	Correlation matrix of level of heavy metals	
	in sediment and water samples location 1 Tunggak River	175
4.35	Pairs of correlation element in sediment sample	176
4.36	Pairs of correlation element in water sample	176
4.37	Pearson's correlation element in water-sediment in location 1	177
4.38	Correlation matrix of level of heavy metals	
	in sediment and water samples location 2 Tunggak River	178
4.39	Pairs of correlation element in sediment sample	179
4.40	Pairs of correlation element in water sample	179
4.41	Pearsons' correlation of element in water-sediment location 2	180
4.42	Correlation matrix of level of heavy metals	
	in sediment and water samples location 3 Tunggak River	181
4.43	Pairs of correlation element in sediment sample	181
4.44	Pairs of correlation element in water sample	182
4.45	Pearsons' correlation of element in water-sediment location 3	183
4.46	Matrix of the principal component analysis loading of metals and	
	major elements of river sediments in location 1 Tunggak River	185
4.47	Matrix of the principal component analysis loading of metals	
	and major elements of river water in location 1 Tunggakk River	186
4.48	Matrix of the principal component analysis loading of metals	
	and major elements of river sediment in location 2 Balok River	189
4.49	Matrix of the principal component analysis loading of metals	
	and major elements of river water in location 2 Balok River	191
4.50	Matrix of the principal component analysis loading of metals	
	and major elements of river sediment in location 3 Balok River	193
4.51	Matrix of the principal component analysis loading of metals	
	and major elements of river water in location 3 Balok River	194
4.52	Enrichment Factors for stream sediments of study area	196
4.53	Contamination Factor and Pollution Load Index	
	of stream sediment	197
4.54	Contamination Factor and Pollution Load Index of stream water	200

LIST OF FIGURES

Figure	No. Title	Page
2.1	Mapping of Location study	28
3.1	Land use mapping in Study Area	41
3.2.	Location 1 in Balok River	42
3.3.	Location 2 in Balok River	43
3.4.	Location 3 in Balok River	44
3.5.	Location 1 in Tunggak River	45
3.6.	Location 2 in Tunggak River	46
3.7	Location 3 in Tunggak River	47
3.8a	Ponar Graph Sampler	48
3.8b	Horizontal water sampler	48
3.9	Inductively Coupled Plasma – Mass Spectrometer (ICPMS)	53
3.10a	Sample Vessel	53
3.10b	Microwave digester equipment	53
3.11	Scheme of Methodology Research	55
4.1	The average chemical oxigent demand values for 3 sampling	
	point along of the Balok River	58
4.2	The average biological oxigent demand values for 3 sampling	
	point along of the Balok River	59
4.3	The average dissolved oxygen values for 3 sampling point	
	along of the Balok River	60
4.4	The average Amoniac Nitrogen values for 3 sampling point	
	along of the Balok River	61
4.5	The average Suspended Solid values for 3 sampling point	
	along of the Balok River	62
4.6	The average pH values for 3 sampling point	
	along of the Balok River	63
4.7	Water Quality Index of sampling site of Balok River performace	64

4.8	Average aluminum values for 3 sampling points	
	of the Balok River systems	66
4.9	Average Chromium values for 3 sampling points	
	of the Balok River systems	67
4.10	Average Manganese values for 3 sampling points	
	of the Balok River systems	68
4.11	Average Chromium values for 3 sampling points	
	of the Balok River systems	69
4.12	Average Nickel values for 3 sampling points	
	of the Balok River systems	70
4.13	Average Copper values for 3 sampling points	
	of the Balok River systems	71
4.14	Average Chromium values for 3 sampling points	
	of the Balok River systems	72
4.15	Average Arsenic values for 3 sampling points	
	of the Balok River systems	73
4.16	Average Cadmium values for 3 sampling points	
	of the Balok River systems	74
4.17	Average Plumbum values for 3 sampling points	
	of the Balok River systems	75
4.18	Al concentrations in sediment of three sampling stations of	
	Balok River during November 2010 until July 2011	78
4.19	Al concentrations in water of three sampling stations of	
	Balok River during November 2010 until July 2012	79
4.20	Cr concentrations in sediment of three sampling stations of	
	Balok River during November 2010 until July 2011	80
4.21	Cr concentrations in water of three sampling stations of	
	Balok River during November 2010 until July 2012	81
4.22	Mn concentrations in sediment of three sampling stations of	
	Balok River during November 2010 until July 2011	82
4.23	Mn concentrations in water of three sampling stations of	
	Balok River during November 2010 until July 2012	83

4.24	Fe concentrations in sediment of three sampling stations of	
	Balok River during November 2010 until July 2011	84
4.25	Fe concentrations in water of three sampling stations of	
	Balok River during November 2010 until July 2012	85
4.26	Ni concentrations in sediment of three sampling stations of	
	Balok River during November 2010 until July 2011	86
4.27	Ni concentrations in water of three sampling stations of	
	Balok River during November 2010 until July 2012	87
4.28	Cu concentrations in sediment of three sampling stations of	
	Balok River during November 2010 until July 2011	88
4.29	Cu concentrations in water of three sampling stations of	
	Balok River during November 2010 until July 2012	89
4.30	Zn concentrations in sediment of three sampling stations of	
	Balok River during November 2010 until July 2011	90
4.31	Zn concentrations in water of three sampling stations of	
	Balok River during November 2010 until July 2012	91
4.33	As concentrations in sediment of three sampling stations of	
	Balok River during November 2010 until July 2011	92
4.34	As concentrations in water of three sampling stations of	
	Balok River during November 2010 until July 2012	93
4.35	Cd concentrations in sediment of three sampling stations of	
	Balok River during November 2010 until July 2011	94
4.36	Cd concentrations in water of three sampling stations of	
	Balok River during November 2010 until July 2012	95
4.37	Pb concentrations in sediment of three sampling stations of	
	Balok River during November 2010 until July 2011	96
4.38	Pb concentrations in water of three sampling stations of	
	Balok River during November 2010 until July 2012	97
4.39	Plot of loading PCA location 1 sediment in Balok River	113
4.40	Plot of loading PCA location 1 water in Balok River	115
4.41	Plot of loading PCA location 2 sediment in Balok River	117
4.42	Plot of loading PCA location 2 water in Balok River	119
4.43	Plot of loading PCA location 3 sediment in Balok River	121

4.44	Plot of loading PCA location 3 water in Balok River	123
4.45	Enrichment Factor (EF) in sediment sites of location Balok River	126
4.46	Contamination Factor sediment of Balok River	128
4.47	Comparison of Sediment Pollution Load Indices	
	of examined streams	130
4.48	Contamination factor in water sampling sites of Balok River	130
4.49	The average chemical oxigent demand values for 3 sampling	
	point along of the Tunggak River	132
4.50	The average biological oxigent demand values for 3 sampling	
	point along of the Tunggak River	133
4.51	The average dissolved oxygen values for 3 sampling point	
	along of the Tunggak River	134
4.52	The average Amoniac Nitrogen values for 3 sampling point	
	along of the Tunggak River	135
4.53	The average Suspended Solid values for 3 sampling point	
	along of the Tunggak River	136
4.54	The average pH values for 3 sampling point	
	along of the Tunggak River	137
4.55	Water Quality Index of sampling site of Balok River performace	138
4.56	Average aluminum values for 3 sampling points	
	of the Tunggak River systems	139
4.57	Average Chromium values for 3 sampling points	
	of the Tunggak River systems	140
4.58	Average Manganese values for 3 sampling points	
	of the Tunggak River systems	141
4.59	Average Chromium values for 3 sampling points	
	of the Tunggak River systems	142
4.60	Average Nickel values for 3 sampling points	
	of the Tunggak River systems	143
4.61	Average Copper values for 3 sampling points	
	of the Tunggak River systems	144
4.62	Average Chromium values for 3 sampling points	
	of the Tunggak River systems	145

4.63	Average Zinc values for 3 sampling points	
	of the Balok River systems	146
4.63	Average Arsenic values for 3 sampling points	
	of the Balok River systems	146
4.64	Average Cadmium values for 3 sampling points	
	of the Balok River systems	147
4.65	Average Plumbum values for 3 sampling points	
	of the Balok River systems	148
4.66	Al concentrations in sediment of three sampling stations of	
	Tunggak River during November 2010 until July 2011	152
4.67	Al concentrations in water of three sampling stations of	
	Tunggak River during November 2010 until July 2011	153
4.68	Cr concentrations in sediment of three sampling stations of	
	Tunggak River during November 2010 until July 2011	154
4.69	Cr concentrations in water of three sampling stations of	
	Tunggak River during November 2010 until July 2011	155
4.70	Mn concentrations in sediment of three sampling stations of	
	Tunggak River during November 2010 until July 2011	156
4.71	Mn concentrations in water of three sampling stations of	
	Tunggak River during November 2010 until July 2011	157
4.72	Fe concentrations in sediment of three sampling stations of	
	Tunggak River during November 2010 until July 2011	158
4.73	Fe concentrations in water of three sampling stations of	
	Tunggak River during November 2010 until July 2011	159
4.74	Ni concentrations in sediment of three sampling stations of	
	Tunggak River during November 2010 until July 2011	160
4.75	Ni concentrations in water of three sampling stations of	
	Tunggak River during November 2010 until July 2011	161
4.76	Cu concentrations in sediment of three sampling stations of	
	Tunggak River during November 2010 until July 2011	162
4.77	Cu concentrations in water of three sampling stations of	
	Tunggak River during November 2010 until July 2011	163

4.78	Zn concentrations in sediment of three sampling stations of	
	Tunggak River during November 2010 until July 2011	164
4.79	Zn concentrations in water of three sampling stations of	
	Tunggak River during November 2010 until July 2011	165
4.80	As concentrations in sediment of three sampling stations of	
	Tunggak River during November 2010 until July 2011	166
4.81	As concentrations in water of three sampling stations of	
	Tunggak River during November 2010 until July 2011	167
4.82	Cd concentrations in sediment of three sampling stations of	
	Tunggak River during November 2010 until July 2011	168
4.83	Cd concentrations in water of three sampling stations of	
	Tunggak River during November 2010 until July 2011	169
4.84	Pb concentrations in sediment of three sampling stations of	
	Tunggak River during November 2010 until July 2011	170
4.85	Pb concentrations in water of three sampling stations of	
	Tunggak River during November 2010 until July 2011	171
4.86	Plot of loading PCA location 1 sediment in Tunggak River	185
4.87	Plot of loading PCA location 1 water in Tunggak River	187
4.88	Plot of loading PCA location 2 sediment in Tunggak River	189
4.89	Plot of loading PCA location 2 water in Tunggak River	191
4.90	Plot of loading PCA location 3 sediment in Tunggak River	193
4.91	Plot of loading PCA location 3 water in Tunggak River	195
4.92	Enrichment Factor (EF) in sediment sites	
	of location Tunggak River	197
4.93	Contamination Factor sediment of Tunggak River	199
4.94	Comparison of Sediment Pollution Load Indices	
	of examined streams	199
4.95	Contamination factor in water sampling sites of Tunggak River	201
4.96	Comparison of water Pollution Load Indices of examined streams	202

LIST OF SYMBOLS/ ABBREVIATIONS

Al	= Aluminum
As	= Arsenic
AN	= Ammoniac Nitrogent
Cd	= Cadmium
Cr	= Chromium
Cu	= Copper
CF	= Contamination Factor
Cd	= Contamination Degree
Е	= East
EF	= Enrichment Factor
Fe	= Ferrum
FAA	= Flame Atomic Absorption
GF-AA	= Graphite Furnace Atomic Absorption
GPS	= Global Position System
ICP-AE	5 = Inductively Coupled Plasma Emission Spectrometer
ICP-OE	S = Inductively Coupled Plasma Optical Emission Spectrometer
ICPMS	= Inductively Coupled Plasma Mass Spectroscopy
INWQS	= Interim National Water Quality Standard
Mn	= Mangan
Ni	= Nickel
Ν	= North
Pb	= Blumbum/ Lead
ppb	= part per billion
ppm	= part per million (mg/L)
PCA	= Principal Component Analysis
USEPA	= United State Environmental Protection Agency
WHO	= World Health Organization
Zn	= Zinc

CHAPTER 1

INTRODUCTION

1.1 Background

Water is a valuable source for the survival of human beings. Man has used water systems for numerous purposes such as drinking, irrigation, fisheries, industrial processes, transportation and waste domestic disposal. Increasing of urbanization, agricultural and industrial practice brings an adverse effect on both surface and ground water such as rapidly decreasing of the water quality (Vazquez et al., 2003), in term of its physical, chemical and biological characteristics. Therefore it can be deduced that water pollution is not any longer an emerging threat.

In Malaysia, the rapid growth of development over the last three decades has overstressed the river system. Currently many rivers in Malaysia have been deteriorated due to aforementioned factors which have exerted immense pressures on water quality. In kuantan, Pahang, particularly in the area of Balok and Tunggak River, the industrial activities based on petrochemical and the expanding residential area have been identified as the contributor to the pollution occurred of a thousands of chemicals that pollute water quality, heavy metals are among the most dangerous groups due to their potential toxicity (Carreras *et al.*, 2009).

This study was conducted to assess and monitoring the present of heavy-metal pollution in the Balok River and Tunggak River as an impact of activity in Gebeng industrial area and resident around the river. Gebeng is the small town and central industry in Kuantan, Pahang, Malaysia. This area is thriving on the hub of profitable activity where many multinational corporations in the petrochemical sector are based there. Waste waters from industry always discharge to the Balok River and Tunggak River through channels than flows toward to South China Sea. Resident of Balok Perdana has a huge sewer as domestic sewerage discharges to the Balok River. Tunggak River receives the effluent from a resident of Balok Makmur and Gebeng Industry area. For this reason, environmental monitoring has become recognized as being vitality important in detecting where insidious pollution occurring. Based on data from JPS that Balok River is about 10 km length and 5 km width, and Tunggak River is about 7 km length and 4.2 km width.

1.2 Problem Statement

The presence of heavy metals in the river system has been long acknowledged to pose to the river water. They are accumulated in the sediment for a long time and therefore pose a further toxic to the whole aquatic environment in contact with water. Under certain condition, metals accumulated in sediments could be release to the overlying waters and thus been further taken up by the organisms (Sing *et al.*, 2005).

Currently for Pahang state unfortunately the information about river water quality is scanty not fairly enough with the rapid industrialization activities. Thus, this study is carried out in order to analyses and monitors the occurrence of heavy metal contamination of water and sediment of Balok River and Tunggak River.

1.3 Objective of the research

The aim of this study is to provide and establish a baseline data of heavy metal occurrence for future references of Pahang rivers, particularly Balok River and Tunggak River, the rivers which are located at Gebeng area and receives the discharges from the industrial activities as well as from the community activities such as from Kampung Balok. The objective of this study can be summarized as the following:

 To determination the concentration of heavy-metal in water and sediment at Balok River and Tunggak River following the discharge from the industry and residential activities.

- 2. To compare the concentration of heavy metals obtained in this study to the Interim National Water Quality Standard (INWQS) for Malaysia.
- 3. To study the distribution of heavy metals between water and sediment by using ANOVA.
- 4. To identify the sources of pollution by using Principal Component Analysis (PCA), Enrichment Factor (EF), Contamination Factor (CF) and Pollution Load Index (PLI).



CHAPTER 2

LITERATUR REVIEW

2.1 Heavy Metal

Metals are natural constituents of rocks and soils and after the environment as a consequence of weathering and erosion (Forstner, 1989). They are often characterized and distinguished from nonmetals by their physical properties, the ability to conduct heat, and its electrical resistance that is directly proportional to temperature, malleability, ductility and even luster (Sherameti and Varma, 2010; Housecroft and Sharpe, 2008; Muller, 2007). It has long been known that, in the right concentrations. Many metals are essential to life and ecosystems (Morgan and Stumm, 1964; Butt et al., 1964; Yunice et al., 1968; Salanki et al., 1992), however chronic exposures to metals can lead to severe environmental and health effects (Handovsky, 1926; Lamb, 1964; Wahlberg, 1965; Hecker et al., 1974; Nriagu, 1988). In general, main metal threats are normally associated with heavy metals such as lead, arsenic, cadmium and plumbum. Unlike many organic pollutants, which eventually degrade to carbon dioxide and water, heavy metals will tend to accumulate in the environment, particularly in lake, arsenic, or marine sediments (Long et al., 1995). As heavy metals are believed to connect with environmental deterioration and quality of human life, therefore an increasing number of countries have signed treaties to monitor and reduce heavy metal pollution (OECD, 1996) in the environment.

The presence of increasing levels of metals in the environment is causing serious concern in public owing to the toxicity shown by the majority of them (Forster and Wase, 1997; Ledin, 2000), most of them have toxic effects on living organisms even at low concentrations and persistence in the environment (MacFarlane and Burcherr, 2000; Carreras, 2009; Sakan *et* al., 2009). In general heavy metals are emitted into the

environment in different ways, i.e. transportation from one location to another, through release from the process in industry, through burning of fossil fuels, process in agricultural, and other human activities (Aksoy *et al.*, 2000). Their concentrations in the environment are of big concern due to their serious effect through the food chain on animals and person health. Thus, the determination of heavy metals concentration in surface water is very important in order to evaluate their potential toxicity to the aquatic habitats.

2.2 The characteristic of heavy metal

2.2.1 Aluminum

Aluminum represent 8% of the earth's crust and it is high abundant in the environment where it is can be found in most rocks (Lide, 2005; Staley and Haupin, 1992). Aluminum is a silvery, white metal. It is ductile and malleable, non-magnetic and noncombustible (IAI, 2007). It's Chemical Abstract Service (CAS) registered number is 7429-90-5. It is the thirteenth element in the periodic system, with atomic number 13 and a relative atomic mass of 26.98. Its melting point is 660°C and its boiling point is 2467°C. The density is 2.7 g/cm³. In moist air, a protective oxide coating of aluminum oxide is formed on its surface (Lide, 2005; O'Neil et al., 2001). For the most part, aluminum compounds are insoluble in water except under strongly acidic or alkaline conditions (Martell and Motekaitis, 1989). Aluminum compounds exist primarily in an ionic form in the environment, and they are not expected to volatilize. The naturally occurring stable isotope is 27Al. The isotope 26Al has a long half life but a low natural abundance and is used as a tracer in biological studies (Jouhanneau et al., 1994). The small ionic radius (54 pm) and the electric charge gives Al^{3+} a strong polarizing effect on adjacent atoms; indeed, aluminum is too reactive to be found free in nature, where aluminum exists only in the oxidation state Al^{3+} (Giordano et al., 1993; Martin, 1991). Aluminum compounds are used in many diverse and important industrial applications such as alums (aluminum sulfate) in water-treatment and alumina in abrasives and furnace linings (Lewis, 2001; O'Neil et al., 2001). They are found in consumer products such as antacids, astringents, buffered aspirin, food additives, and antiperspirants (Lewis, 2001; Lione, 1985; O'Neil et al., 2001).

Powdered aluminum metal is often used in explosives and fireworks (O'Neil et al., 2001). Aluminium has harmful effects on the different developmental stages of fish in acidic water (e.g., Vourinen et al. 1990, Weatherley et al. 1992, 1993, 19944a, 1994b). During long-term exposures in aluminum-containing acidic water, the spawning of fish can be delayed (Beamish et al. 1975, Tam and Payson 1986, Rask et al. 1992). The presence of Al in natural water system is also of major concern because of its potential threat to the health of number of species including human (Lewis 1989). Aluminum is known to be toxic to the central nervous systems and play a role in causing analysis encelophathy and dialysis oesteodystrophy (Alfery et al., 1976; Savory and will 1991). Aluminum could be mobilized from soil and sediment by both natural weathering and accelerated acidification process, resulting in detectable concentrations in surface waters (Adomako et al., 2008). Due to the exceptionally slight solubility of Aluminum in water, its content in waters is very low, ranging from 60 to 300 µg/l at pH 5-9. In river water, it average 64 μ g/l in sea water it is about 1-5 μ g/l, while in water of open oceans it amounts to only 0.5 µg/l. Increased acid rain falls have caused acidification of surface water in many areas, which in turn have resulted in mobile aluminum release from metastable compounds in bottom sediments and their transition into water. A pH drop to 6.0 leads to dying out of snails and bivalves; a further decrease to pH 5.5 brings death to more sensitive insects e.g. mayfly pupas and caddis-fly larvae; pH below 5.0 kills trout and below 4.0 exterminates eels. Lowering pH to 4.0 causes dying out of less sensitive insect and plankton, while at pH 3.0 some water plants disappear. It is evident that a disturbance of ecological balance in the ecosystem is conveyed through food chain to terrestrial organisms (birds), which elicits further disadvantageous changes in the whole biocenosis (Kotoeski et al., 1995; Matczak, 1995).

2.2.2 Chromium

Chromium (Cr) is one of the less common elements and does not occur naturally in the elemental form, but only in the compound. Chromium (Cr) is mined as a primary one product in the form of the mineral chromite, FeCr₂O₄. Major sources of chromium (Cr) contamination include releases from electroplating process and the disposal of chromium containing waste (Evanko & Dzombak, 1997). Generally, chromium (Cr) was found in nature primarily as chromite ore with chromium (Cr) in the trivalent (Cr (III)) form. Anhydrous chromium nitrate is a chemical with the molecular formula Cr $(NO_3)_3$, a molecular mass of 238.01 g/mol and the Chemical Abstract Service (CAS) registry number 13548-38-4. The nonahydrate form $(Cr(NO^3)^3 \cdot 9H^2O)$ has a molecular mass of 400.21 g/mol and a Chemical Abstract Service (CAS) registry number 7789-02-8. In recent years, contamination of the environment by chromium (Cr), especially hexavalent chromium, has become a major area of concern. The contamination of aquatic environment by toxic metals, such as chromium (Cr) and plumbum (Pb) is of great concern due to their trends to accumulate on vital organs of humans and animals (Alan *et al.*, 2007; Gholivand *et al.*, 2007), could enter the human body when breathing, eating, or drink water containing chromium.

Furthermore, chromium salts are used in chemical analysis, tanning, dying, ceramics, and in the dyestuffs industry. The major uses of chromium are in the metallurgical industry for the production of stainless steel and other alloy steels, and in the refractory. Other uses are in the electroplating, metal finishing and leather tanning industries and in the production of fungicides, pigments, oxidants, and catalysts and in the glass and photographic industries (Stoeppler, 1992).

Trivalent chromium, Cr (III), is a pollutant commonly found in wastewater produced from leather tanning, dye, and wood preservation and electroplating industries (Han *et al.*, 2006). Cr (III) is thought to be an essential nutrient required for sugar and fat metabolism in organisms (Anderson, 1997). However, long time exposure causes skin allergic, cancer and deoxyribonucleic acid (DNA) damage (Yun *et al.*, 2001; Park *et al.* 2006; Ulouzlu *et al.* 2008). Moreover, chromium (III) is toxic to fish when its concentration in water exceeds 5.0 mg L⁻¹ (Alloway and Ayres, 1997 and Ulouzlu *et al.* 2008). Chromium is mined as primary ore products in the form of the mineral chromite, FeCr₂O₄. Main sources of chromium contamination include releases from electroplating processes and the disposal of chromium containing wastes (Evanko & Dzombak, 1997). Chromium can be transported by surface runoff to surface at waters in its soluble or precipitated form. Most of the chromium released into natural waters is the particle associated. However, and is ultimately deposited on the sediment (Smith *et al.*, 1995). Chromium is extensively used in industries, like electroplating, paint and pigment manufacturing, textile, fertilizer, and leather tanning (Gangguli and Tripathiu, 2002). Many industries discharges trivalent and hexavalent chromium with waste effluent to the soil and surface water. Chromium, which is generated by various industries, occurs in different oxidation states but Cr (III) and Cr (IV) are the most significant. Hexavalent chromium is acutely toxic, mutagenic, and carcinogenic (Lee *et al.*, 2008). Low-level exposure can cause kidney and liver damage, and can damage circulatory and nerve tissue. Chromium often accumulates in aquatic life, adding to the danger of eating fish that may have been exposed to high level chromium.

2.2.3 Manganese

Manganese is an abundant element comprising about 0.1% of the earth's crust (Graedel, 1978). It does not occur naturally as a base metal, but is a component of over 100 minerals, including various sulfides, oxides, carbonates, silicates, phosphates, and borates (NAS, 1973). Manganese exists in both inorganic and organic forms. An essential ingredient in steel, inorganic manganese is also used in the production of drycell batteries, glass and fireworks, in chemical manufacturing, in the leather and textile industries and as a fertilizer. The inorganic pigment known as manganese violet (manganese ammonium pyrophosphate complex) has nearly ubiquitous use in cosmetics and is as well found in certain paints. Organic forms of manganese are used as fungicides, fuel-oil additives, smoke inhibitors, an anti-knock additive in gasoline, and a medical imaging agent. Metallic manganese (ferromanganese) is used principally in steel production to improve hardness, stiffness, and strength. It is used in carbon steel, stainless steel, high-temperature steel, and tool steel, along with cast iron and super alloys (EPA, 1984; NAS, 1973). Manganese compounds have a variety of uses. Manganese dioxide is commonly used in production of dry-cell batteries, matches, fireworks, porcelain and glass-bonding materials, amethyst glass, and as the starting material for production of other manganese compounds (EPA, 1984; NAS, 1973; Venugopal and Luckey, 1978). Manganese chloride is used as a precursor for other manganese compounds, as a catalyst in the chlorination of organic compounds, in animal feed to supply essential trace minerals, and in dry-cell batteries (EPA, 1984). Manganese sulfate is used primarily as a component of fertilizer (60% of total consumption) and as a livestock supplement (30% of total consumption); it is also used in some glazes, varnishes, ceramics, and fungicides (EPA, 1984; Windholz et al. 1983).

Potassium permanganate's oxidizing power allows it to be used as a disinfectant; an anti-algal agent; for metal cleaning, tanning, and bleaching; and as a water purification agent (Lewis, 2001). Another common source of manganese is found in the street drug "Bazooka." It is a cocaine-based drug contaminated with manganese-carbonate from free-base preparation methods (Ensing, 1985).

The toxicity of manganese is known to increase with increasing water hardness (Howe et al. 2004) and elevated Manganese (and iron) levels could be a good indicator of hypolimnetic water that is likely to negatively impact upon macroinvertebrate communities (Scullion et al.1982; Brittain & Saltveit 1989). Correlative studies have linked high manganese levels in deep water reservoir discharges with declining fish health (Grizzle 1981). This is the reason why manganese belongs to highly toxic heavy metals. It can also affect the ecosystem negatively, accumulating in the food chain. Common sources of toxic manganese levels in the environment include sewage discharges, acid mine leachates, sediment-pore water and hypolimnetic reservoir releases (Howe et al. 2004). Manganese (and iron) levels can also affect the composition and biomass of freshwater algal communities (Wetzel 1983). Algal communities have a significant influence on the rivers ecology and can impact upon aesthetic and recreational values. For instance, filamentous growths can detract from a swimming experience and the proliferation toxic cyanobacteria is a potential public health issue.

2.2.4 Ferrum

Iron (Ferrum) has an atomic number of 26, an atomic mass of 55.85 amu, a melting point of 1538°C, and it is found in Group VIII-B on the periodic table. Iron is the second most abundant metal in the earth's crust (exceed only by Al) and is found in igneous, sedimentary, and metamorphic rocks. Fe is a silvery-white, hard, brittle, fairly fusible, and ductile. Furthermore, ferrum is one of the three naturally magnetic elements, other are cobalt and nickel. Ferrum has four allotropic from an alpha, beta, gamma and delta. The alpha form is magnetic, but when transformed into the beta form. The magnetism disappears. The pure of Ferrum is very reactive chemically, and rapidly corrodes, especially in moist air or at elevated temperatures.

UMP

These iron particulates are then spread through precipitation, wind, and volcanic activity throughout the globe. Iron (Ferrum) is mined worldwide and is used in a variety of industries, especially in the production of steel and steel alloys, as a fertilizer, and as a fungicide. Iron is also used to process bauxite, which is the ore where aluminum is extracted. The Anthropogenic sources of iron are a result of atmospheric deposition from steel production furnaces, onto land through foundries and mines, and as wastewater from steel plants and runoff from agricultural areas using iron based fertilizers (Oehme, 1979; Lottermoser, 2007). Iron is an essential element in the bodies of all vertebrates, as it is used in the formation of hemoglobin and is found in countless enzymes. Iron has been used medicinally to treat acne, hemorrhoids, gout, edema, and fevers (Oehme, 1979). Toxicity to iron in humans is a result of habitual inhalation and through ingestion of food; however, this is of lesser concern than iron deficiency. One important indirect effect of iron on humic river ecosystems, in particularly, may be its effects on light condition, and consequent impact on primary production and species interaction affected by the quality and quantity of light (Cotton & Wilkinspon, 1980; Heikkinen, 1990c). The combined direct and indirect effects of iron contamination decrease the species diversity and abundance of periphyton, benthic invertebrates and fishes. Sorption and co-precipitation of metals by Fe-oxides decrease the bioavailability and toxicity of water-borne metals, but may increase the dietary supply of metals and lead to toxic effects along the food (Kari, 1995).

2.2.5 Nickel

Nickel (Ni) is a common and potentially toxic tracing metal in many freshwater ecosystems (Chowdhury *et al.*, 2008, Cempel and Nikel, 2006). Pure nickel is a hard, silvery-white metal. It can release into the environment by volcanoes, forest fires, weathering of rocks, vegetation, and anthropogenic sources such as steel production and electroplating (Cempel and Nickel, 2006; Muyessen *et al.*, 2004; USEPA, 1986). Nickel can enter streams and water bodies through a natural weathering and erosion process as well as by settling of atmospheric nickel emissions. Waterborn nickel frequently accumulates in sediment river. Nevertheless, nickel levels in surface water are normally very low (often undetectable). While Nickel is released to the atmosphere by windblown dust, volcanoes, combustion of fuel oil, municipal incineration, and

UMP.

industries involved in nickel refining, steel production, and other nickel alloy production.

Pure nickel is a hard, silvery-white metal, which has properties that make it very desirable for combining with other metals to form mixtures called alloys. Some of the metals that nickel can be alloyed with are iron, copper, chromium, and zinc. These alloys are used in making metal coins and in industry for making items such as valves and heat exchangers. Most nickel is used to make stainless steel. There are also compounded consisting of nickel combined with many other elements, including chlorine, sulfur, and oxygen. Many of these nickel compounds are water soluble and green in color. Nickel and its compounds have no odor or taste. Nickel compounds are used for nickel plating, to color ceramics, in batteries elements, and as catalysts that increase the rate of chemical reactions.

The 24^{th} the most abundant element in the Earth's crust, Ni is relatively widespread in the environment (Doig and Liber 2007; Cempel and Nikel, 2006). It occurs naturally at concentrations between 1 and 10 µg/L but may reach as high as 1000 ppm in areas impacted by activities such as mining or smelting (Eisler, 1998). Nickel (Ni) is a common metal in freshwaters and one of the toxicants that present in the environment. The general harmful health effect of nickel in human is an allergy reaction. The serious harmful effects from exposure to nickel, such as chronic bronchitis, reduce lung function, and cancer of the lung and nasal sinus, have occurred in people who have breathed duct containing certain nickel compound while working in nickel refineries or nickel processing plants. Nickel can enter the human body when breathe air containing nickel, when drink water or eat food that contains nickel. The amount of nickel inhaled that reaches human lungs and enters the blood depends on the size of the nickel particles. If the particles are large, they stay in the body. Lawrence et al (2004) reported negative effect of Nickel in aquatic life on abundance of phototropic organisms like Algae and Cyanobacteria.

2.2.6 Copper
Copper is a metallic element that occurs naturally as the free metal, or associated with other elements in the compound that comprise various minerals. Copper is primarily used as a metal or an alloy (e.g., brass, bronze, gun metal). Industrial manufacturers, processors, and users of copper and copper compounds are required to report the quantities of this substance released to environmental media annually (EPA, 1988d). Factory's releases are only a fraction of the total environmental releases of copper and copper compounds. Other sources of copper release into the environment originate from domestic waste water, combustion processes, wood production, phosphate fertilizer production, and natural sources (e.g., windblown dust, volcanoes, decaying vegetation, forest fires, sea spray, etc.) (Georgopoulos et al., 2001; Harrison, 1998). The Copper can enter your body when you drink water or eat food, soil, or other substances that contain copper. Copper particulates are released into the atmosphere by windblown dust, volcanic eruptions, and anthropogenic sources, primarily copper smelters and ore processing facilities. Copper is released into waterways by natural weathering of soil and rocks, disturbances of soil, or anthropogenic sources (e.g., effluent from sewage-treatment plants). (Salomons and Fo"rstner, 1984) mention that copper is a common contaminant in coastal waters, particularly in industrialized bays and estuaries. After mercury and silver, copper is considered the most toxic metal to a wide spectrum of marine life (Clark, 1997), hence its value in antifouling preparations. Automobile fluid leaks, junkyards, cooling water discharges, copper containing pesticides, water distribution pipes, road transportation, vehicle brakes, metal plating, roofs, refineries, metal processing and related industries, smelting operations are sources of copper contamination in the environment (Hauri, 2001). Sediment is an important sink and reservoir for copper. Sediment generally contains <50 ppm copper. The level can reach several thousand ppm in polluted areas (Harrison and Bishop, 1984).

Copper (Cu), a trace metal and essential for cellular metabolism, may become extremely toxic for aquatic animals as its concentration increase in water (Carvalho & Fernandes, 2006). The impact of Cu on the aquatic environment is complex and depends on the physicochemical characteristic of water (Laure'n & McDonal, 1986; Mazon & Fernandes, 1999; Tao *et al.*, 1999; Takasuki *et al.*, 2004). Alkalinity, hardness and pH strongly influence Cu specification in water and consequently its

bioavailability to fish (Florence *et al.*, 1992; Playle *et al.*, 1992; Erickson *et al.*, 1996; Tao *et al.*, 2000, 2001). The use of copper can kill algae, fungi, and molluscs demonstrated that it is highly toxic to aquatic organisms. In fact, copper is one of the most toxic metals to aquatic organisms and ecosystems. This is just one of the reasons that environmentally sensitive mining practices are so important (MINING, 2009)

2.2.7 Zinc

Zinc is one of the most common elements in the earth's crust and an essential nutrient in humans and animals that is necessary for the function of a large number of metalloenzymes. Zinc is found in the air, soil, and water and is present in all foods. It is released to the environment both from natural and anthropogenic sources; however, releases from anthropogenic sources are greater than those from natural sources. The primary anthropogenic sources of zinc in the environment (air, water, soil) are related to mining and metallurgic operations involving zinc and use of commercial products containing zinc. Zinc salts have numerous applications and are used in wood preservation, catalysts, photographic paper, and vulcanization acceleration for rubber, ceramics, textiles, pigments, and batteries. Deficiency leads to inhibition of growth, suppression of appetite, impaired immune to infection and abnormalities in fetal development (Mills, 1986). In higher doses, zinc may cause copper deficiency. Acute toxic effects from excessive zinc intake have been noted but are very uncommon (Maret *et al*, 2005).

Zinc has been associated with impairment of river and stream water quality for many years. For example, the State of Texas (2005) reported rivers as not meeting their aquatic uses due to toxic metals; Wichita and Middlefork Rivers lost their aquatic uses due to selenium, Neches River below Lake Palestine due to lead, and Neches River above Lake Palestine due to high level of Zinc. Peplow (2000) reported that elevated concentrations of Cadmium, Copper, Selenium including Zinc in stream waters and sediments reduced species diversity and abundance in aquatic communities.

Opinions on zinc toxicity to water organisms vary. It depends to a considerable extent on the ion form of zinc occurrence, calcium presence and magnesium, as well as

pH of the water. Dissolved zinc toxicity (Meinck *et al.*, 1997; Pistelok and Galas, 1998) depends on the salt where it is incorporated. Zinc sulfate is considerable more toxic than zinc chloride. It also depends on water hardness. Adverse effects are increased distinctly in soft water. Zinc is toxic for fish (Dojlidio, 1987) at the level of 0.1 mg Zn/dm³. The concentration inhibits self-purification process. LC50 of zinc for fish is $0.5-5.0 \text{ mg Zn/dm}^3$. According some other data, zinc in concentration exceeding 3.0 mg Zn/dm³ inhibits aerobic purification process and kills protozoa at the level of 20 mg Zn/dm³, first of all ciliates (Meinck *et al.*, 1997; Pistelok and Galas, 1998).

2.2.8 Arsenic

Arsenic is an element that is widely distributed in the earth's crust at an average concentration of 2–5 mg/kg, and is primarily associated with igneous and sedimentary rocks in the form of inorganic arsenic compounds (Tamaki and Frankenberger, 1992). Elemental arsenic is ordinarily a steel grey metal like material which sometimes occurs naturally. However, arsenic is usually found in the environment combined with other elements such as oxygen, chlorine, and sulfur. Arsenic occurs naturally in rocks, soil, plants and animals (EPA, 2007). Arsenic may be released to water from the natural weathering of soil and rocks, and in areas of volcanism. Arsenic may also leach from soil and minerals into groundwater. Anthropogenic sources of arsenic releases to water include from industrial and agricultural activities, particularly from wood preservatives, fertilizers, pesticides, animal feeding operations, and mining activities (EPA, 2007), nonferrous metals, especially copper, smelting, waste water, dumping of sewage sludge, coal burning power plants, manufacturing processes, urban runoff, atmospheric deposition and poultry farms (Nriagu and Pacyna, 1988; Pacyna *et al.*, 1995). Arsenic is found in the earth's crust at an average level of 2 ppm (NAS, 1977b).

Arsenic in soil may originate from the parent materials that form the soil, industrial wastes, or use of arsenical pesticides. Geological processes that may lead to high arsenic concentrations in rock and subsequently, the surrounding soil included hydro thermic activity and pegmatite formation (Peters *et al.*, 1999). Historically, arsenic was used in pesticides on cotton and orchards, and some forms continue to be used on cotton today (ATSDR, 2007). Additionally, increased alkalinity (increased pH)

may increase the levels of arsenic in groundwater because it dissolves naturallyoccurring arsenic in surrounding rocks and soils (WHO, 2003). Thus, arsenic can get into lakes, rivers, or underground water by dissolving in rain or snow or through the discharge of industrial wastes. Some of the arsenic will stick to particles in the water or sediment on the bottom of the lakes or river, and some will be carried along by the water. Ultimately most arsenic ends up in the soil or sediment. Although some fish and shellfish take in arsenic which may be build-up in tissues, most of this arsenic is in a form (often called "fish arsenic") that is less harmful. Arsenic is found naturally in the environment. You may be exposed to arsenic by eating food, drinking water, or breathing air. Children may also be exposed to arsenic by eating dirt. You may as well be exposed by skin contact with soil or water that contains arsenic. All types of arsenic exposure can cause kidney and liver damage, and in the most severe exposure, there is erythrocyte hemolysis (Hoekman, 2008). Contact to arsenic causes arsenicosis, chronic arsenic poisoning. An early indication of arsenicosis is hyperpigmentation which may develop after only a few years of exposure (Sampson et al., 2008). Longer-term As exposure causes skin cancer, acute myocardial infarction and several forms of internal cancer, such as cancers of the lung, bladder and kidney (Hopenhayn, 2006; Yuan et al., 2007).

Toxicity and bioaccumulation of arsenic are strongly depend on its chemical state, in particularly its chemical specification (Moore and Ramamoorthy, 1984; Philips, 1990; Mori 1999). Trivalent and pentavalent in organic ionogenic forms of As can exist dissolved in natural water, as well as organic forms. According to Spehar *et al.* (1980) the inorganic forms is the most toxic and its bioaccumulation is more significant.

2.2.9 Cadmium

Cadmium is an element that presents naturally in the earth's crust. Pure cadmium is a soft, silver-white metal. Mainly sources of cadmium in the aquatic environment are from natural weathering processes, mining, metal smelters, industries, agricultural use of sludges, fertilizers and pesticides, burning of fossil fuels, and the deterioration of galvanized materials and cadmium-plated containers (Anon b, 1996). Cadmium is a non-essential metal that is toxic even when present in very low

concentrations. The toxic effect of cadmium is exacerbated by the fact that it has an extremely long biological half-life and is therefore retained for long periods of time in organisms after bioaccumulation (Webb, 1975; Fianko *et al.*, 2007).

Use of cadmium, its alloys, and its compounds are used in a variety of consumers and industrial materials. The use of cadmium compounds falls into five categories: active electrode materials in nickel-cadmium batteries (70% of total cadmium use); pigments used mainly in plastics, ceramics, and glasses (12%); stabilizers for polyvinyl chloride (PVC) against heat and light (17%); engineering coatings on steel and some nonferrous metals (8%); components of various specialized alloys (2%) (Elinder, 1992; IARC, 1993; Thornton, 1992; USGS, 1997).

Small amounts of cadmium enter the environment from the natural weathering of minerals, forest fires, and volcanic emissions, but most is released by human activities such as mining and smelting operations, fuel combustion, disposal of metal-containing products, and application of phosphate fertilizer or sewage sludges (Elinder, 1985a). Cadmium may be released to water by natural weathering processes, by discharge from industrial facilities or sewage-treatment plants, or by leaching from landfills or soil (EPA, 1981, 1985a; IJC, 1989). Cadmium may also leach into drinking-water supplies from pipes in the distribution system (Elinder, 1985a). A large proportion of the cadmium load in the aquatic environment is due to diffuse pollution originating from many different sources rather than from point sources. Land disposal of cadmium-containing wastes (including batteries), land application of sewage sludge, and the use of phosphate fertilizers are the principal sources of cadmium releases to soil (Elinder, 1985a; EPA, 1985d; IARC, 1993).

Cadmium is extremely toxic to fish. Its effects on the growth rate have been observed even for concentration between 5 and 10 μ /l (Green *et al.*, 1986; Masoud *et al.* 2004). Phytoplanktons are likely to play a more significant role in scavenging of cadmium than they play in the removal of other metals (Price and Calvert, 1973; Masoud et al. 2004).

Increasing water temperature (from 8° to 12° C) increased the rate of cadmium and zinc toxicity in Bull trout and rainbow trout (Hansen et al. 2002). Cadmium

accumulates in the kidney, liver, and gills of freshwater fish (Chowdhury et al. 2004; Dallinger et al. 1996; Thomas et al. 1985; Norey et al. 1990a; Kraal et al. 1995). Cadmium accumulation in these organs appears to be related to the presence of cadmium-binding molecules called metallothioneins (Dallinger et al. 1996; Carpene and VaSik, 1989; Hogstrand et al. 1991).

There is evidence that a high accumulation of cadmium in fish (Arctic char) might be the result of increased metal absorption in the gills from the water due to low alkalinity (Dallinger et al.1996; Wograth and Psenner 1995; Isock et al. 1995). Alkalinity plays a role in what and where cadmium and other metals accumulate, such that liver metallothionein was dominated by copper and zinc in spite of high cadmium levels in the kidney (Dallinger et al. 1996). The role of metallothionein in fish accumulation is well demonstrated (See e.g. Dallinger et al. 1996 and Yudkovski et al. 2008). As a result, in the Bristol Bay waters, which tend to have low alkalinity (Northern Dynasty Mines 2005), fish may uptake environmental cadmium at a higher rate than in comparable higher alkalinity waters.

Ambient water quality criteria for cadmium (and chromium III, copper, lead, nickel, silver, and zinc) for the protection of aquatic life are based on water hardness. Cadmium's acute toxicity decreases with increasing water hardness (Niyogi et al. 2008; Calamari et al. 1980; Davies et al. 1993; Brinkman and Hansen 2007). Water pH also influences the toxicity of cadmium but is not considered in ambient water quality criteria (Hansen et al. 2002). As a result, water quality standards for a given location or stream must also consider the fish species present, water quality, and life stages (See Hansen et al. 2002). The effects of pH on acute cadmium toxicity are largley unknown (Niyogi et al. 2008; Playle et al. 1993). There are some indications that low pH may actually protect some fish against acute cadmium toxicity (Niyogi et al. 2008). It is important to understand the effects of pH independent of other surrogate variables (Niyogi et al. 2008).

Consuming fish or other animals that have accumulated cadmium may pose a threat to human health. In one study, cadmium concentrations in catfish muscle tissue increased with increasing concentrations in their food (and significantly reduced fish growth) (Ruangsomboon and Wongrat, 2006). The study further demonstrated that a low level of cadmium in water may not indicate that fish living in those waters is safe for human consumption.

2.2.10 Plumbum (Pb)

Plumbum (Pb) is a heavy, low melting, bluish-gray metal that occurs naturally in the Earth's crust. However, it is rarely found naturally as a metal. It is usually found combined with two or more other elements to form plumbum compounds. In natural Pb is found to be in the form of substances, such as, PbSO₄ or plumbum sulfide. Minerals that contain Pb as one of their components are galena, cerussite anglesite, pyromophite, wulfine, and crocite is usually found together with Zn, Fe, Cd and Hg (Rilley, 1980). 40% of Pb is used for producing batteries while the rest of it is utilized for welding, producing pipes, making metal alloy that composes of inorganic components of tin, producing rust preventing paint, making ceramics, and it can also be used as a stabilizer in the production of PVC. The most important organic substance of Pb is tetraethyl Pb, which is added in benzene fuel in order to prevent the knocking of engines.

Plumbum may be used in the form of metal, either pure or alloyed with other metals, or as chemical compounds. The commercial importance of lead is based on its ease of casting, high density, low melting point, low strength, ease of fabrication, acid resistance, electrochemical reaction with sulfuric acid, and chemical stability in air, water, and soil (King and Ramachandran, 1995; Shea, 1996; Sutherland and Milner, 1990).

Plumbum is used in the manufacture of storage batteries; lead alloys used in bearings, brass and bronze and some solders; sheets and pipe for nuclear and X-ray shielding, cable covering, noise control materials; chemical resistant linings; ammunition; and pigments and lead compounds used in glass making, ceramic glazes, plastic stabilizers, caulk, and paints. Consumption of lead in lead-acid batteries, including SLI (Start, Light, Ignition) batteries used in cars, trucks, and other vehicles and industrial type, lead acid batteries is the major use of lead today (ATSDR, 2005). Lead is commonly found in soil, especially near roadways, older houses, old orchards,

and mining areas, industrial sites, near power plants, incinerators, landfills and hazardous waste sites.

Exposure to plumbum can result in a wide range of biological effects depending on the level and duration of exposure. Various effects occur over a broad range of doses, with the developing young and infants being more sensitive than adults. Lead poisoning, which is so severe as to cause evident illness, is now very rare. For as is known, plumbum fulfills no essential function in the human body, it can merely do harm after uptake from food, air or water. Plumbum is a particularly dangerous chemical, as it not only accumulates in individual organisms, but also in entire food chains.

2.3 Toxicity of Heavy Metal

When considering the different kinds of contamination, heavy metals are especially dangerous because of their persistence and toxicity (Adriano, 2001). Its activities may save implication to the quality of agricultural soil, such as phytotoxicity at high concentrations and may transfer of heavy metals to the human diet from crop uptake or soil ingestion by grazing livestock (Nicholson et al., 2003).

In general metals are able to transfer from soil to the other ecosystems component, such as underground water or crops, and therefore affect may human health through the water supply and food web. From the literature, among various pollutants, heavy metals are consider as the most toxic, persistent, and abundant compounds that can accumulate in aquatic habitats and their concentration increases through a bio magnification (Sin et al., 2001, Kishe and Machwa, et al., 2003, Ahmed et al., 2005). A long term waste water irrigation that contains heavy metals may lead to the accumulation of heavy metals in agricultural soils and plants (Mapanda *et al.*, 2005; Nan *et al.*, 2002; Gupta *et al.*, 2008). Potential health risk to the human make the food safety issue one of the most serious public concern (Cui *et al.*, 2004). It has been reported that vegetables accumulate heavy metals in their edible and nonedible parts.

Although some of the heavy metals such as Zn, Mn, Ni and Cu act as micronutrients at lower concentrations, however they may become toxic at higher concentrations. It has been shown that crops and vegetables grown in soils contaminated with heavy metals have greater accumulation of heavy metals than those grown in uncontaminated soil (Marshall et al. 2007; Sharma et al. 2006, 2007). In human, intake of vegetables is an important path of heavy metal toxicity through the dietary intake of contaminated vegetable with heavy metals may lead to various chronic diseases.

Intawongse & Dean (2006) through his work has assessed the bioavailability of Cd, Cu, Zn and Mn in the human gastrointestinal tract from the edible part of vegetables using an in vitro gastrointestinal (GI) extraction technique. His study reported the lettuce and radish were found to be more responsible than other vegetables for the accumulation of heavy metals in humans through the edible portion. It is believed that the absorption capacity of heavy metals depends upon to the nature of vegetables in which some of them may have a greater potential to accumulate higher concentrations of heavy metals than others.

Meanwhile, Duruibe et al. (2007) suggested that bio-toxic effects of heavy metals depend upon the concentrations and oxidation states of heavy metals, kind of sources and mode of deposition. Severe exposure of Cd may result in pulmonary effects such as emphysema, bronchiolitis and alveolitis. Renal effects may also result due to subchronic inhalation of Cd (European Union 2002; Young 2005). Pb toxicity causes reduction in the haemoglobin synthesis, disturbance in the functioning of kidney, joints, reproductive and cardiovascular systems and chronic damage to the central and peripheral nervous systems (Ogwuegbu & Muhanga 2005). Higher concentration of Zn cause impairment of growth and reproduction (Nolan 2003).

The effects of heavy metal compounds on aquatic birds have been a widely studied topic in ecotoxicological studies. However the studies animals especially mainly focus on the postnatal period of life, it is believed that exposure may already take place earlier, during embryonic development (Lovvorn and Gillingham, 1996; Heinz *et al.*, 1999; Spahn and Sherry, 1999; Hoffman *et al.*, 2000). The eggs of waterfowl may come into direct contact with different surface water pollutants (Hatan and Hatano, 1992).

During the breeding season pollutants on the breast feathers, feet, or nesting materials of aquatic birds may be transferred to their eggs, causing embryonic death, growth impairment and/or teratogenicity. The effects of such exposure of the eggs to different petroleum and crude oils, effluents and solvents have been extensively reported (Hoffman, 1990 and Kertesz & Fancsi *et al.*, 2003).

All of heavy metals are believed to be potentially harmful to most of organisms at some level of exposure and absorption. However, it is very interesting that some of these small amounts of these elements are essentia and are actually necessary for good health, unfortunately in large amount, they may cause acute or chronic toxicity (poisoning). Heavy metals such as cadmium, mercury, lead, copper, and zinc, are regarded as serious marine pollutants because of their toxicity, high tendency to be incorporated into food chains, and huge ability to remain in an environment for a long time (Eaton, 1995; Puyate, et al., 2007; Bello and Alabi, 2005; Hoekman 2008). Heavy metal toxicity can damage or reduced mental and central nervous functions, lower energy level, and damage to blood composition, lungs, kidney, liver, and other vital organs. The most serious toxic heavy metals Cr, Ni, Pb, Cd, and As. Cr (VI), Ni and Cd are carcinogenic; and the health effects of Pb included neurological impairment and malfunctioning of the central nervous systems (Markus and McBratney, 2001; Nadal, Schuhmacher and Domingo, 2004). Nevertheless, certain organisms are of special interest because they possess in ability to survive under a condition of metal's contamination, which would prove toxic to other living things (Antonovics et al., 1997), with increasing use of a wide variety of metals in industry on the daily life.

2.4 The occurrence of heavy metal in surface water

Water is essentials to supports plant and animal life (Vanloon and Duffy, 2005), and it is generally obtained from two principal natural sources; Surface water such as fresh water lakes, rivers, streams, etc. and Ground water such as borehole water and well water (McMurry and Fay, 2004; Mendie, 2005). Much literature mentioned that heavy metals are the common waste products of increasing of anthropogenic activities and their emission often results in the pollution of the surrounding environment (Agoramoorthy et al., 2008). Being discharged directly to the surface waters, constituents of industrial effluents create a significant hazard to aquatic ecosystems (Ko and Baker, 2004; Tusseau-Vuillemin *et al.*, 2007; Focazio *et al.*, 2008; Schwarzbauer and Ricking, 2010; Botalova & Schwarzbauer, 2011). The levels of certain trace elements in rivers, lakes and other water systems have been found to be moderate, very, and high as a result of industry discharges (Al-Masri *et al.*, 2002; Coker *et al.*, 1995). Contamination of aquatic ecosystems with heavy metals has seriously increased worldwide caution level, and a lot of studies have been published on the heavy metals in the aquatic environment (Wagner and Boman, 2003).

Environmental pollution with toxic metals is becoming a global phenomenon because heavy metals are extremely toxic, and they are present in our environment. Problem association with the dumping of sewage and uncontrolled industrial discharges are rising in the regions. These situations happen because lack of effective environmental legislation and monitoring exacerbates the problem as does the reliance of large section of the population on coastal resources such as shellfish, high population and industrial building near the river system. Heavy metal contamination in a marine coastal environment is correlated to sources of population in the nearby estuarine and rivers. All of metal concentrations are generally transported to the marine environment by rivers through estuarine. River transportation is likely the dominant pathway through which heavy metals enter lake ecosystems (Radakovitch et al., 2007; Lin et al., 2008; Yang et al., 2009). In most circumstance, the major contribution of anthropogenic metals in a marine coastal area is of global origin, i.e. from mining, industrial, and urban development, and other human activities near rivers and estuaries (Morton and Blackmore, 2001; Clark, 2001; Vazquez et al., 2003; Ives and Cardinale 2004; Petrovic et al., 2004; Ip Carman et al., 2007). Heavy metals are widely distributed in nature. They occur in soil, surface water, plants, air and various forms of an organism through various pathways as a result of anthropogenic activity (Larison et al., 2000; Frignani and Bellucci, 2004; Rainbow, 2004; Demirak et al., 2006; Binell et al., 2008). Heavy metals pollution of water resources, aquifers and wetland system caused by industry, agriculture and municipally treated wastewater is a worldwide problem as an impact of development of a country for increasing quality of life. River, lakes, channels, oceans and ground water are often contaminated by a variety of heavy-metal substances that can have adverse effects on aquatic life and pose risks to human life. These pollutants

are straight released by industrial plants and municipal sewage treatment plants, other come from polluted runoff in urban and agricultural areas and some as the result of historical contamination, which in turn increases the concentration of nutrients along with other wastes in the marine environment (Reddy *et al.*, 2003; Zhou *et al.*, 2004; Begum, 2009; Hang *et al.*, 2009). For this reason, environmental monitoring has become recognized as being vitally important in detecting where insidious pollution is occurring. The pollutants involved and sources from which they came. Therefore, the influence of anthropogenic traced inputs on coastal areas needs further research. Moreover, the distribution of heavy metals from river system through estuaries and coastal areas also need more understanding.

Tuna *et al.*, 2007 have been studeid about seasonal variation of the concentrations of trace metals (Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn) were measured by ICP-AES in the water and sediment from the Saricay Stream, Geyik Dam and OrtakoyWell in the same basin. Comparisons between trace metal concentrations in water and sediment in three sources (Stream, Dam and Well) were made. The concentrations of a large number of trace metals in the water and sediment were generally higher in the Stream than in the Well and Dam, particularly in summer. Trace metal concentration ranges in sediments of the Saricay Stream and its sources showed very wide ranges (as mass ratio): Co: $5-476\mu g g^{-1}$, Cr: $15-1308\mu g g^{-1}$, Cu: $7-128\mu g g^{-1}$, Fe: $1120-13210\mu g g^{-1}$, Mn: $150-2613\mu g g^{-1}$, Ni: $102-390\mu g g^{-1}$, Pb: $0.7-31.3\mu g g^{-1}$ and Zn: $18-304\mu g g^{-1}$, whereas Cd was not detected. Trace metal concentration ranges found in waters were: Co: $9.5-20.7\mu g L^{-1}$, Cr: $20.3-284\mu g L^{-1}$, Cu: $170-840\mu g L^{-1}$, Fe: $176-1830\mu g L^{-1}$, Mn: $29.3-387\mu g L^{-1}$, and Ni: $4.3-21.9\mu g L^{-1}$.

The west coast of Peninsular Malaysia including the southern part of the peninsula is an area where industries and populations are concentrated (Yap et al. 2002). The southern part of Peninsular Malaysia becomes important when the Ninth Malaysia Plan covering the period 2006 to 2010 was launched in March 2006. It identified the newly named Iskandar Development Region (IDR) as one of the catalyst and high-impact development areas under the Plan. The IDR is a new main southern development corridor in Johore and it will greatly enhance the development of Malaysia. Yap et al., 2011 also studeid about surface water quality in the Malaysian coastal waters. Coastal

water samples were collected from 20 sampling sites in the southern part of Peninsular Malaysia. Seven physico-chemical parameters were measured directly in-situ while water samples were collected and analysed for 6 dissolved trace metal concentrations. The surface water (0-20 cm) physico-chemical parameters including temperature, salinity, dissolved oxygen (DO), pH, total dissolved solids (TDS), specific conductance (SpC) and turbidity while the dissolved trace metals were Cd, Cu, Fe, Ni, Pb and Zn. The ranges for the physico-chemical parameters were 28.07-35.6°C for temperature, 0.18-32.42 ppt for salinity, 2.20-12.03 mg/L for DO, 5.50-8.53 for pH, 0.24-31.65 mg/L for *TDS*, 368-49452 µS/cm for SpC and 0-262 NTU for turbidity while the dissolved metals (mg/L) were 0.013-0.147 for Cd, 0.024-0.143 for Cu, 0.266-2.873 for Fe, 0.027-0.651 for Ni, 0.018-0.377 for Pb and 0.032-0.099 for Zn.

Ochieng *et al.*,2007 have been studeid about the concentrations of heavy metals Ag, Cd, Co, Cr, Cu, Mn, Ni, Pb, Sn and Zn were analysed in water of five Rift Valley lakes Nakuru, Elementaita, Naivasha, Bogoria and Baringo in Kenya. The dissolved mean concentration levels (lg/L) in water ranged within 13.0–185.0 (Ag), 2.0–43.0 (Cd), 5.0–316.0 (Co), 25.0–188.0 (Cr), 4.7–100.0 (Cu), 50.0–282.0 (Mn), 19.0– 288.0 (Ni), 25.0–563.0 (Pb), 300.0–1050.0 (Sn) and 29.0–235.0 (Zn).

2.5 The accumulated of heavy metal in surface sediment

Sediments are composed of all detritus, inorganic or organic particles eventually settling on the bottom of a body of water. They originate from soil erosion and precipitation from chemical and biological processes in the water. Sediment geological are at the end of the path for natural and anthropogenic materials, which is the root of contaminated problems (Burton, 1992).

Heavy metals are regarded hazardous not only due their toxicity potential even in small amounts but also due to their capability to bioaccumulate, which refers to the increase in concentration of a chemical in an organism over time, compared to their concentration in the environment. Once the heavy metals enter to the aquatic environment, they are distributed among the aqueous phase, suspended particles, and sediments (Pertsemli and Voutsa, 2007). Suspended particles play an important role controlling the reactivity, transport and biological impacts of metals and other substances in the aquatic environment and provide a crucial link for chemical constituents between water column, bed sediments and food chain (Pertsemli and Voutsa, 2007; Turner and Milward, 2002). As sediment is a common name for the soil particles that are carried by a river or flood and then settle when the flow velocity slows, a rapid urbanization and industrialization, have always introduced heavy metals to the estuarine and coastal sediments (Apitz *et al.*, 2005). In general, sediments are the principal sink for heavy metals in the aquatic environment (Izquierdo *et al.*, 1997; Sin *et al.*, 2001; Jha *et al.*, 2003; Akcay, 2003; Marissa *et al.*, 2008; Korfali and Jurdi, 2011), thus they are usually as environmental indicators to reflect the history of pollution of a river or marine systems (K.P. Singh *et al.*, 2005; Leonardo *et al.*, 2006; Zhang, 2008).

Recently, Salati and Moore (2010) reported the occurrence of Cd, 0.1–2 mg/kg; Zn, 33.9–101.1 mg/kg; Pb, 29.6–199.1 mg/kg; Ni, 95.9–123.6 mg/kg; Mn, 200–263 mg/kg; Cu, 19.7–63.4 mg/kg; Cr, 114–253 mg/kg; and Sc, 3.3– 4.3 mg/kg in sediment from Khoshk River Iran. Meanwhile, a study conducted in Yangtze River China founded that the concentration of heavy metal in sediment were Hg, 0.165 mg/kg; Cd, 0.04 mg/kg; Pb, 44.17 mg/kg; Cr, 71.00 mg/kg; Cu, 49.33 mg/kg; Zn, 218.33 mg/kg; As, 21.52 mg/kg (Yujun, 2008).

In Malaysia, through a study performed by Saraee *et al.*, 2010, the researcher found the concentration of As, 7.1 to 25.5 mg/kg; Cd, 0.1 to 0.4 mg/kg; Cr, 35.9 to 79.2 mg/kg; Cu, 4.6 to 16.8 mg/kg; Hg, 0.05 to 5.0 mg/kg; Ni, 15.9 to 20.9 mg/kg; Pb, 20.9 to 64.8 mg/kg; and Zn, 4.4 to 79.5 mg/kg in the surface sediment of the east coast of Peninsular Malaysia. Present of high heavy metal in surface sediment because the east of Peninsular Malaysia covered by agriculture, industry, fertilizer in agriculture include arsenic. Finally, it is important to recognize that the concentrations of arsenic, cadmium, chromium, copper, mercury, nickel, lead and zinc as recorded in the studied surface sediments of the east coast of peninsular Malaysia constitute the natural background levels of the system.

Yap *et al.*, 2011 studied about heavy metal accumulated in surface sediments were collected from the north western aquatic area (13 intertidal sites and 5 river drainages) of Peninsular Malaysia, which were suspected to have received different

anthropogenic sources. These sites included town areas, ports, fishing village, industrial areas, highway sides, jetties and some relatively unpolluted sites. The present study revealed that 4.79–32.91 µg/g dry weight for Cu, 15.85–61.56 µg/g dry weight for Pb, and 33.6–317.4 μ g/g dry weight for Zn based on 13 intertidal surface sediments while those based on 5 river drainage surface sediments were $10.24-119.6 \,\mu g/g$ dry weight for Cu, 26.7–125.7 µg/g dry weight for Pb and 88.7–484.1 µg/g dry weight for Zn. In general, the metal levels in the drainage sediments are higher than in the intertidal sediments, suggesting dilution factor in the intertidal sediment and direct effluent from point sources in the drainage sediment. A study by Navar et al. (2004) indicated intensive dredging, reclamation, construction, and shipping activities in the Ponggol Estuary of Singapore (east of Johor Strait) may have led to resuspension and bioavailability of particulate elements. They reported presence of Sn, Pb, Ni, Cd and Cu in particulate- and dissolved fractions and sediments whose were ranges were from n.d.-92 lg/g, n.d.-303.2 lg/g, n.d.-2,818.4 lg/g, n.d.-74.4 lg/g and n.d.-1,117.7 lg/g, respectively. Consequently, toxic elements released from sediments may prove poisonous to the organisms that may have accumulated including bacteria (Nayar et al. 2004).

A study by Zulkifli (2004) evaluate current status of trace elements contamination in the surface sediments of the Johor Strait for element Fe, Zn, Cu, Cr, Pb, V, As, Ni, Co and Cd. The result mainly Iron ($2.54 \pm 1.24\%$) was found as the highest occurring element, followed by those of zinc (210.45 ± 115.4 lg/g), copper (57.84 ± 45.54 lg/g), chromium (55.50 ± 31.24 lg/g), lead (52.52 ± 28.41 lg/g), vanadium (47.76 ± 25.76 lg/g), arsenic (27.30 ± 17.11 lg/g), nickel (18.31 ± 11.77 lg/g), cobalt (5.13 ± 3.12 lg/g), uranium (4.72 ± 2.52 lg/g), and cadmium (0.30 ± 0.30 lg/g), respectively. This area is an important area because of the existence of mangroves, sea grasses, corals and mudflats ecosystems. It is also important in other aspects. These include the high population estimated at around 3 million people (DSM, 2002), fish and selfish resources, new petrochemical port, and the latest of the new and larger economic zone (Iskandar Malaysia). These features are expected to enhance and accelerate "high impact" development (industrial, urban, agriculture, atc.) in this area. As for the city-state of Singapore, much of the lands have developed into industrial-, urban-, agriculture- and aquaculture areas (Ismail, 2008). Massive development along

both sides of the strait could lead to significant physical- and chemical changes in the environment.

Although sediment analyses do not represent the extent of toxicity, they are useful to assess the burden anthropogenic component above and beyond the lithogenic background and also in some instances, trace the sources of pollution long after input has taken the place (Frignani *et al.*, 1997; Fukue *et al.*, 1997; Tokalioglu *et al.* 2000; Buccolieri *et al.*, 2006).

2.6 Study Area

In Malaysia, as same as other countries in the world, the level of metal pollution of freshwater bodies, particularly the rivers, is no longer within safe limits for human consumption. The water quality status of rivers in Malaysia has always been a cause for concern for various local authorities, government agencies as well as the public at large. Rivers in Malaysia are generally considered to be polluted with coherent examples such as Sg. Galing, Sg. Balok and Sg. Tunggak in Kuantan, Pahang. From physical observation alone, one can deduce that something is not right with the current water quality condition of these rivers. From a scientific perspective though, it is still necessary to quantify the degree of pollution, in order to manage the pollution issues in a systematic and optimised fashion.

Gebeng is a small town and central industrial area in Kuantan, Pahang, Malaysia. The Gebeng Industrial Estate is a thriving hub of profitable activity where many multinational corporations in the petrochemical sector are based there. Wastewater after treatment always discharges to the Balok River (Figure 2.1), and then flows toward to South China Sea. It is therefore, imperative to determine the impact activity Gebeng industrial area for environment of Balok River and Tunggak River. Besides that, there are many residential establish around this area mainly Balok Perdana, Balok Makmur, Balok Seberang resident, etc., which always discharged domestic waste to Balok and Tunggak River. Based on data JPS that beams length Balok River about 10 km and width 45 m this area divide into three locations, which is considered to be the main disposal site. However, for Tunggak River length, 7 km and width 42 m these areas also divide into three important locations.



Figure 2.1. Mapping of study location (sources Google Map)

2.7 Multivariate Analysis

Multivariate statistical analysis methods such as principal component analysis (PCA), ANOVA, correlation analysis, an enrichment factor and Pollution Load Index, have been applied to indicate the degree of contamination by heavy metals from lithogenic and anthropogenic sources (Aksu *et al.*, 1998; Kazi *et al.*, 2009; Loska and Wiechula, 2003Rubio *et al.*, 2001; Simeonov *et al.*, 2001; Santos *et al.*, 2005; El Nemr *et al.*, 2006; Pekey, 2006; Zhang *et al.*, 2007; Yin *et al.*, 2010).

Multivariate statistical analysis is a useful technique for identifying common patterns in data distribution, leading to a reduction of the initial dimension of data sets and facilitating its interpretation (Castellano *et al.*, 2007). Regarding metal pollution, these techniques have been applied to identify natural or anthropogenic sources in

sediments (Liu *et al.*, 2004), urban soils (Abillino *et al.*,2002; Manta *et al.*, 2002; Zhang *et al.*, 2006 and Lee *et al.*, 2006) agricultural soils (Facchinelli *et al.*, 2001; Mico *et al.*, 2006; Martin *et al.*, 2006; and Huang *et al.*, 2007).

1. Pearson's Correlation (*r*)

Correlation coefficients are used in statistics to measure how strong a relationship is between two variables. There are several types of correlation coefficient: Pearson's correlation or <u>Pearson correlation</u> is a **correlation coefficient** commonly used in linear regression. Pearson's correlation coefficient can be used to measure the degree of correlation between the metal data and can provide suggestive information regarding heavy metal sources and pathways (Manta *et al.*, 2002; Al-Khasman and Shawabkeh, 2006; Yang *et al.*, 2011).

The quantity r, called the *linear correlation coefficient*, measures the strength and the direction of a linear relationship between two variables. The linear correlation

coefficient is sometimes referred to as the *Pearson product moment correlation coefficient* in honor of its developer Karl Pearson.

The mathemical formula for computing r is:

$$r = \frac{n\sum xy - (\sum x)(\sum y)}{\sqrt{n(\sum x^2) - (\sum x)^2}\sqrt{n(\sum y^2) - (\sum y)^2}}$$

where n is the number of pairs of data.

- The value of *r* is such that $-1 \le r \le +1$. The + and signs are used for positive linear correlations and negative linear correlations, respectively.
- Positive correlation: If x and y have a strong positive linear correlation, r is close

to +1. An r value of exactly +1 indicates a perfect positive fit. Positive values

indicate a relationship between x and y variables such that as values for x increases,

values for *y* also increase.

Negative correlation: If x and y have a strong negative linear correlation, r is close

to -1. An r value of exactly -1 indicates a perfect negative fit. Negative values indicate a relationship between x and y such that as values for x increase, values for y decrease.

- No correlation: If there is no linear correlation or a weak linear correlation, r is close to 0. A value near zero means that there is a random, nonlinear relationship between the two variables.
- Note that r is a dimensionless quantity; that is, it does not depend on the units employed.
- A *perfect* correlation of ± 1 occurs only when the data points all lie exactly on a straight line. If r = +1, the slope of this line is positive. If r = -1, the slope of this line is negative.
- A correlation greater than 0.8 is generally described as *strong*, whereas a correlation

less than 0.5 is generally described as *weak*. These values can vary based upon the

"type" of data being examined. A study utilizing scientific data may require a stronger correlation than a study using social science data.

Many researcher using correlation coefficient between two or three element for to identification relathionship element. Pearson's correlation coefficient can be used to measure the degree of correlation between the logarithms of the metal data (Garcia and Millan, 1998). Pearson's correlation coefficient can be used to measure the degree of correlation between concentrations of the metals. Li *et al.* 2011 have been analyzed the correlation coefficients of metal contents in samples of Chaohu Lake, Anhui, China. High correlation coefficients (>0.65) were found among Cr, Ni, Cu, and Zn, indicating that the origin of metals is related to the polluted rivers which are connected with the Chaohu Lake Anhui, China. No significant correlation was found between Cd and other five metals, while a negative correlation was found between Hg and any other metals, indicating a different source for Hg.

Study by Seref Keskin (2011) analysis Pearson's correlation coefficients among the contents of metal concentrations (Mo, Cu, Pb, Zn, Ni, Co, Mn, Fe, Cr, As, V and Cd), grain size, organic carbon and carbonate contents metals in sediments of Akkaya Dam to identification the extent of environmental pollution and to discuss the origin of these contaminants in sediments of dam. Kanann *et al.*, 2008 also using Pearson's correlation coefficient analysis concentration Cd, Cr and Pb that accumuted in water, sediment and seaweed (*ulva lactuca*) in the Pulicat Lake, South East India. Bam *et al.*, 2011 have been used Pearson correlation coefficient matrix of the 16 elements (K, Ca, Ti, Fe, Mn, Zn, Cu, Zr,Sr, Y, Pb, V, Cr, Ga, Ni and Rb) and the physiochemical characteristics measured for the soils in Densu river Basin, Ghana.

2. Principal Component Analysis

To measurement and understanding of the dynamic of pollution indicator parameters in an area has been enhanced with the application of basic and advanced statistical methods. In recent times, multivariate statistical methods such as principal component analysis (PCA) is being used in treatment of pollution data (Soares *et al.*, 1999; Ip *et al.*, 2007; Marques *et al.*, 2008; Salati and Moore, 2010; Zhang *et al.*, 2010; Yang *et al.*, 2011). The principal component analysis (PCA) was used as a chemometrical approach to reduce the size of the variable space and substitute a large number of parameters by a small number of independent factors (principal components), which allows data interpretation and data structure explanation (Martinez *et al.*, 2006, 2009; Delvalls *et al.*, 1998).

Song *et al.*,2009 have been used a bivariate correlation analysis to evaluate the regional correlations of the water quality parameters, while the principal component analysis (PCA) technique was used to extract the most influential variables for regional variations of river water quality of a tributary of the Pearl River, the Beijiang, Southern China. Six principal components were extracted in PCA which explained more than 78% and 84% of the total variance for agricultural/rural and industrial/urban areas, respectively. Wenchuan *et al.*, 2001 have been used Principal Component Analysis (PCA) to assess the degree of contamination and spatial distribution of heavy metals and nutrients in different areas of Taihu Lake, China.

These applications of different multivariate statistical technique help in the interpretation of complex data to improve understand the environmental and ecological condition of the studied area. Many studied associated with these methods have been carried out. Environmental applications of PCA are varied and widespread, and the technique has been applied to surface and ground waters (e.g. Chen *et al.*, 2007; Kuppusamy and Grirdhar, 2006; Salati and Moore, 2010), soil (Boruvka *et al.*, 2005; Zhang 2006; Wang and Wu, 2008; Yang *et al.*, 2011), sediments (e.g. Soares *et al.*, 1999; Ip *et al.*, 2007; Reid and Spencer, 2009) and biota (e.g. Yawei *et al.*, 2005). However, increasingly it has also been used to discriminate between contaminant sources (e.g. Kim *et al.*, 2006; Mudge and Duce, 2005; Reid and Spencer, 2009), to identify key variables for environmental monitoring purpose (e.g. Carlon *et al.*, 2001; Shin and Lam, 2001) and to identify sources of a pollutant (e.g. Ip *et al.*, 2007; Wang and Wu, 2008).

Principal Component Analysis (PCA) is the most common multivariate statistical method used in environmental studies and is employed to extract a small number of latent factors for analyzing relationships among the observed variables (Manta *et al.*, 2002; Han *et al.*, 2006; Lee *et al.*, 20006a; Reid and Spencer, 2009). Principal component analysis is a data reduction technique that aims to give details most of the variance in the data while reducing the number of variables to a few uncorrelated components with retaining important information and representing variables in a form that can be easily interpreted (Loska and Wiechuya, 2003; Lee *et al.*, 2006; Reid and Spencer, 2009). The first principal component (PCA axis 1) is the combination of

variables that explains the greatest amount of variation. The second principal component (PCA axis 2) defines the next largest amount of variation and is independent of the principal component. Computer software programmed such as SPSS, STATISTICA, SAS and R (version 2.4 and current versions) can be used to explore environmental pollution data using PCA.

3. Enrichment Factors

A common approach to estimating the anthropogenic impact on sediments is to calculate a normalized enrichment factor (EF) for metal concentrations above uncontaminated background levels (Salomons and Forstner, 1984; Dickson *et al.*, 1996; Hornung *et al.*, 1989; Abraham and Parker, 2008; Shakeri and Moore, 2010). In the present study, the enrichment factor (EF) was used to assess the level of contamination and the possible anthropogenic impact in the sediments of the Balok River and Tunggak River.

To identify and assessment of anomalous metal concentrations, the geochemical normalization of the metal data to conservative elements, such as Al, Fe, Mn, Sc or Si, is employed (Bergamaschi *et al.*, 2002; Misrha *et al.*, 2004; Yongming *et al.*, 2006; Salati and Moore, 2010). A number of authors successfully used Ferrum to normalize metals contaminants (Schiff and Weisberg, 1999; Baptista Neto *et al.*, 2000; Mucha *et al.*, 2003; Conrad and Chrisholm Brause, 2004; Cevik *et al.*, 2009; Christophoridis et al., 2009; Meza-Figueroa *et al.*, 2009; Bhuiyan *et al.*, 2010; Esen *et al.*, 2010; Ghrefat and Yusuf, 2010). Therefore, in the present study, Ferrum has been used as a conventional tracer to differentiate natural from anthropogenic components. According to Ergin et al., (1991) the metal enrichment factor (EF) is defined as follows:

$$EF = \frac{\left(\frac{M}{Fe}\right)}{\left(\frac{M}{Fe}\right)} \frac{sample}{background}$$

Where EF is the enrichment factor, $\left(\frac{M}{Fe}\right)$ sample is the ratio of metal and Fe concentration of the sample, and $\left(\frac{M}{Fe}\right)$ background is the ratio of metal and Fe concentration of a background.

Trace elements may be immobilized within the stream sediments and thus could be involved in absorption, cou-precipitation, and complex formation (Okafor and Opuene, 2007; Mohiuddin *et al.*, 2010). Heavy metals may enter into aquatic ecosystems from anthropogenic sources, such as industrial wastewater discharges, sewage wastewater, fossil fuel combustion and atmospheric deposition (Linnik and Zubenko, 2000; Campbell, 2001; Lwanga *et al.*, 2003; El Diwani and El Rafie, 2008; Idrees, 2009). To better assess the potential heavy metal enrichment, the use of enrichment factors is suggested (Karageorgis *et al.*, 2009). EF is a good tool to differentiate the metal source between anthropogenic and naturally occurring sources (Morillo *et al.* 2002; Adamo *et al.* 2005; Vald'es *et al.* 2005). EF was calculated to determine if levels of metals in sediments of Balok Rivers were of anthropogenic origins (i.e. contamination). The geochemical normalization was obtained using Fe as the reference element for the following reasons (Daskalakis and O'Connor, 1995): (1) Fe is associated with fine solid surfaces; (2) its geochemistry is similar to that of many trace metals; and (3) its natural sediment concentration tends to be uniform.

Many authors prefer to express the metal contamination with respect to average shale to quantify the amount and degree of metal pollution (Muller, 1969; Forstner and Muller, 1973). In this study, the background concentrations of Al, Cr, Mn, Fe, Ni, Cu, Zn, As, Cd, and Pb were taken from Turekian and Wedepohl (1961) showed in Table 2.1. The world average shale concentrations of elements of interest are either directly measured in texturally equivalent uncontaminated sediments or size fractions or taken from literature (Teng *et al.*, 2004).

Lianfeng (2010) have been studied the contamination of the sediments and soils in Dalian, Northeastern China was assessed on the basis of enrichment factor (EF) and geoaccumulation index for elements Zn, Pb, Cu and Cr. The data reveal elevated concentrations of Cu (16.7-25.3 mg kg-1), Pb (24.2-37.9 mg kg-1) and Cr (64.5- 117 mg kg-1). Except for Zn, other 3 heavy metals have been accumulated (EF>1). The highest EFs of Cu, Pb and Cr are 1.77, 2.16 and 1.89, respectively. Yap *et al.*, 2010 also have been studied enrichment factor analysis for Cu, Pb, and Zn contamination in sediment of north western Peninsular Malaysia. which were suspected to have received different anthropogenic sources. These sites included town areas, ports, fishing village, industrial areas, highway sides, jetties and some relatively unpolluted sites.

Table 2.1 World average shale concentrations (ppm) (Turekian and Wedepohl, 1961) of monitored elements

Sources	Heavy Metal									
	Al	Cr	Mn	Fe	Ni	Cu	Zn	As	Cd	Pb
Shale (ppm)	80000	90	850	47200	68	45	95	13	0.3	20

According to Hernandez *et al.*, 2003, EF values ranging between 0.5 and 2 indicate the metal is entirely from crustal materials or natural process, whereas EF value greater than 2 indicates some enrichment corresponding mainly to anthropogenic inputs. EF can also assist in determining the degree of metal contamination. Five categories are recognized on the basis of EF in Table 2.2 (Sutherland, 2000; Loska and Wiechuya, 2003).

EF<2		Deficiency to minimal enrichment
EF=2-5		Moderate enrichment
EF=5-20	1	Significant enrichment
EF=20-40		Very high enrichment
EF>40		Extremely high enrichment

Table 2.2 Claasification of enrichment factor (Loska and Wiechuya, 2003)

4. Contamination Factor

To assess the excessive values of monitored elements in water samples, the Teng *et al.* (2004) approach was followed using the equation: $Cd = \Sigma Cfi$, Where Cd is the contamination degree, and Cfi is the contamination factor for the i-th element, Cfi = (Cn/Cb)-1, Where, Cn is the analytical value of the i-th element, and Cb is the upper permissible limit of an element in water. In this study, the WHO (2004) guideline values for drinking water quality were selected for the calculation of contamination degrees of the water from streams.

In pollution studies, measured concentrations of various pollutants in the atmosphere, water and soil are normally compared with established set of standards or

guidelines of notable agencies. This comparison process enables researchers to evaluate the pollution status of any vicinity of interest. The standards and guidelines establish the threshold concentrations of the pollutants above which they may pose the danger to the environment. These standards and guidelines may be national or internationally generated by a body of repute comprising experts of the field. The national bodies and international agencies may include the Environmental Protection Agency (EPA) of the various countries, World Bank, International Atomic Energy Agency (IAEA), World Health Organization (WHO) and other environmentally conscious bodies. Table 2.3 is the guidelines values for drinking water quality.

Hoovy Ma	tol	Maximu	m allowable concentrati		tion in drinking water (mg/L)	
neavy wietai			WHO*		EPA**	
Aluminum			0.2		0.05 - 0.20	
Arsenich			0.01		0.01	
Cadmium			0.03		0.005	
Chromium			0.05		0.1	
Copper			2		1.3	
Ferrum			1-3		0.3	
Mangan			0.4		0.05	
Nickel			0.07		0.1	
Plumbum			0.01		0.015	
Zinc			5		5	

Table 2.3 Guidelines for drinking water quality.

Sources: World Health Organization (2004) Sources: Environmental Protection Agency (2006) **

5. **Pollution Load Index (PLI)**

Pollution Load Index is used to find out the mutual pollution effect at different stations by the different elements in soils, water and sediments (El-Sammak and Abdul-Kassim, 1999). The PLI of a sampling point, community or an area is obtained by deriving Contamination Factors (CFs), using background concentrations or baseline or concentration of the element of interest in an unpolluted area (Tomlinson et al, 1980; El-Sammak and Abdul-Kassim, 1999; Adomako et al., 2008; Adokoh et al., 2010). The CF of an element is the ratio of its concentration in sample and base concentration. The CFs for sediment was calculated using the following equation:

CF = element concentration in soil / background value in the earth shale.

The CF in the sediment sample, which gives an indication of the presence and concentration of particular contaminants, was computed for the sediment using their average elemental concentrations and the maximum corresponding with the world shale values of abundance metal in the earth crust (Turekian and Wedepohl, 1961) presented in Table 2.1. Description of CF and PLI and their pollution intensities are listed in Table 2.4. Table 2.4. CF and PLI values with their pollution grade and intensitas

	Grade	Intensity	
CF value			
<1.2	I	Unpolluted area	
1.2 - 2	II	Lightly polluted area	
2 - 3	III	Moderately polluted are	
>3	IV	Heavily polluted area	
PLI value			
<0	1	Unpolluted	
1	2	Baseline levels of pollutant present	
>100	3	Progressive deterioration of environment	

Sources: Nyarko et al. (2004) for CF Yaqin et al. (2008); and Tomlinson et al. (1980); Nyarko et al. (2006); Angulo (1999) for PLI

The resultant CFs of the elements were used to compute the PLIs measure of the mutual pollution effect on the soils (Tomlinson *et al.*, 1980; Cabrera *et al.*, 1999; Adomako *et al.*, 2008 and Adokoh *et al.*, 2010) as follows:

PLI sampling site = $\sqrt{[3]}$ CF_{PT} x CF_{PD} x CF_{RH}

A number of contamination factors will be derived for different metals at each sampling site, and a sites pollution load index may then be calculated by multiplying the contamination factors and deriving the Nth root of the N factors (Tomlinson *et al.*, 1980). Pollution Load Index value of 1 indicates heavy metal load close to the background level, and value above 1 indicates pollution (Tomlinson *et al.*, 1980; Cabrera *et al.*, 1999).

6. Interim National Water Quality

The main causes of river pollution are usually due to lack of awareness and the attitude of people. It shown through waste water effluent from domestic sewage (Bell, 1971; Pande and Shot, 1980), agricultural activity (Atsushi *et al.*, 2005) and animal husbandry (Brix and Schierup, 1989) along river corridors. Malaysian government has arranged various steps including drafting policies, rules and programmed to reduce river water quality, marine ecology and water catchment area (Department of Irrigation and Drainage Malaysia, 2005).

In 1985, the government undertook a national study dubbed the "Development of Water Quality Criteria and Standards for Malaysia", whose researchers consisted of a multidisciplinary team of experts from universities throughout the country. The study was carried out in four phases with the intention of developing a national "benchmark" of water quality conditions on a per parameter basis. The study had to be carried out, as just adopting foreign criteria to local conditions would not be suitable due to differences in environmental characteristics and climatology. A good case in point is the solubility of oxygen. In Malaysia, oxygen solubility is limited by our equatorial climate; cool climate countries in turn, tend to have higher oxygen solubility (DOE, 1985).

The study orientation was on the beneficial uses of water which was focused on, water for domestic water supply, fisheries and aquatic propagation, livestock drinking, recreation and agricultural use (Sawyer, 2003). Over 120 physico-chemical and biological parameters were reviewed in the study and, in the end, the INWQS was drafted. The INWQS defined six classes (I, IIA, IIB, III, IV and V) referred to for classification of rivers or river segments based on the descending order of water quality vis-a-vis Class I being the "best" and Class V being the "worst" (Apendix A-17).

Class I represented water body of excelent quality. Standards are set for the conservation of natural environment in its undisturbed state. Water bodies such as those in the national parks areas, fountainheads, and in high land and undisturbed area come under this category where strictly no discharge of any kinds is permitted. Water bodies in this category meet the most stringent requirements for human health and aquatic life protection.

Class II A represented water bodies of good quality. Most existing raw water supply sources come under this category. In practise, no body contact activity is allowed in this water for prevention of probable human pathogens. There is a need to introduce another class for water bodies not used for water supplay but of similiar quality which may be referred to as Class IIB. The determination of Class IIB standard is based on criteria for recreational use and protection of sensitive aquatic species. Class III is defined with the primary objective of protecting common and moderately tolerant aquatic species of economic value. Water under this classification may be used for water supply with extensive or advanced treatment. This class of water is also defined to suit livestock drinking needs.

Class IV defined water quality required for major agricultural irrigation activities which may not cover minor application to sensitive crops and finally. Class V represents other water which do not meet any of the above use.



CHAPTER 3

MATERIALS AND METHOD

3.1 Introduction

This chapter describes the materials, and the methodologies used for heavy metal pollution assessment in the Balok and Tunggak River system and its aquatic habitats. In addition to that the rational of the selection of monitoring station I, II, and III, analysis are explained in this chapter.

3.2 Selection of Monitoring Stations

Potential sites for monitoring stations were observed prior to commencement of sampling. The observation identified conducted industrial activities, land use patterns and humans activities that may possible impact the river water quality and the aquatic habitats at the proposed sampling station.

The sampling stations of the Balok River and Tunggak River as well as, its land use pattern at the surrounding of both rivers are illustrated in figure 3.1. The selections of sampling stations were based on the following criteria:

- 1) Accessibility and ability to sample under all weather conditions;
- 2) Homogeneity of the water column
- 3) The aquatic habitats present at the site;
- 4) The main tributaries combination the river;
- 5) Location of industrial areas, residential and other activities human.



Figure 3.1 Land use mapping in Study Area (Google Map)

All the sampling locations coordinate were recorded its using a GPS (Global Position System) instrument (Data label in lab). All the location details are explained in section 3.2.1 to 3.2.2.

Table 3.1	Sampling	location
-----------	----------	----------

River	Sampling station	Location	Coordinate
Balok River	1	Downstream Nyior River	$N = 03^{\circ} 56' 38,8'',$ E = 103° 22' 10.5''
	2	Sewage of Balok Perdana resident	$N = 03^{\circ} 57' 14.8'',$ E = 103° 21' 59,6''
	3	Sewage of Industrial Gebeng Area	N = 03° 57' 51.2", E = 103° 21' 56,3"
Tunggak River	1	Sewage of Kampung seberang Balok Resident	N = 03° 57' 28,1", E = 103° 23' 06.2"
	2	Sewage of Balok Makmur Resident	N = 03° 57' 33.4", E = 103° 23' 10.2"
	3	Sewage of Balok Makmur Resident and near chipboard factory	N = 03° 57' 39.2", E = 103° 23' 14.5"

3.2.1 Location of sampling station at Balok River

I. Sampling Station (Location) 1: Downstream Nyior River



Figure 3.2. Location 1 in Balok River

The first sampling point at Balok River, located at the downstream of Nyior River (Figure 2.2). This area received domestic waste water from human activity upstream of the Nyior River. It is where Kp Balok Baru resident and a few large scale industries is located. Form the observation, an access to this sampling site is limited due to its location is in an indigeneous forest managed by Jabatan Kehutanan Pahang. In general, according to Department of Environment (DOE), Pahang, the average width of the Nyior River was ± 20 m, and beams 11.3 km. The banks were mostly vegetated by indigenous forest. Marginal vegetation was minimal. Fallen trees and logs provided extra habitat for macroinvertebrate colonization and fish refuge.

II. Sampling Station (Location) 2: Sewage of Balok Perdana resident



Figure 3.3. Location 2 in Balok River

For the second sampling point, the location is a big drain receive disposal from municipal and industrial activities before discharge into the river (Figure 3.3). This point is surrounded by a large housing area like Balok Perdana Resident and some other resident, very little shop houses operating as small scale industries for wood processing, food processing and engineering companies. From the observation, there is also a lot of fishing activities have been carried out at this point. III. Sampling Station (Location) 3: Sewage of Industrial Gebeng Area



Figure 3.4. Location 3 in Balok River

Third sampling point of this location received wastewater from industrial Gebeng area (Figure 3.4). This point is surrounded by many large scale industries such as chemical, electronics, electroplating, battery, printing, paper, boxes, paint, and car and also motorcycle workshops as well as food stalls. This site is also near a rural residential area. Marginal vegetation was very sparse and dominated by trees.

3.2.2 Location of sampling station at Tunggak River

- <image>
- I. Sampling Station (Location) 1: Downstream Nyior River

Figure 3.5. Location 1 in Tunggak River

This site was selected as the first monitoring site in the upper reaches of the Tunggak River because it is located at the downstream of extensive pipes that convey waste water from municipal Kampung Seberang Balok resident and Gebeng industry area to the river (Figure 3.5). The river's banks were partly eroded and vegetated characterized by grassland with some overhanging vegetation. Many human activities in this area like fishing crab and fish raising ponds.

II. Sampling Station (Location) 2: Sewage of Balok Makmur Resident



Figure 3.6. Location 2 in Tunggak River

Meanwhile, the second sampling location (Balok Makmur resident) is located beside a settlement and some lorry body work and car repair workshops that are operating actively (Figure 3.6). From the observation, the river is polluted with domestic wastes contributed by an existing due to a squatter settlement at this sampling point and also due to the urban and industrial run-off, farmland, cattle grazing area and a dumping site. Sedges, reeds and aliens trees characterized as the marginal vegetation. III. Sampling Station (Location) 3: Sewage of Balok Makmur Resident and near chipboard factory



Figure 3.7. Location 3 in Tunggak River

This was selected as the monitoring station for the lower catchment of Tunggak River as the site receives all the runoff from the urban settlement and the surrounding informal settlements (Figure 3.7). This point of the river is now surrounded by many industries such as electronics, printing, paper, boxes, paint, garment, car and motorcycle workshops, food, electroplating, battery and other industries. Marginal vegetation was predominantly sedges, grasses and trees.

3.3. Materials

3.3.1 Equipment and Instrument

Glassware that is petri-dish, reaction tube, backer glass, measurement flash, measurement glass, Erlenmeyer, balance bottle, volumetric pipette and funnel. The
equipment included in this research were such as Global Position Systems (GPS), digital balance, oven, centrifuge, micro pipette 100 μ l - 1000 μ l, blender (Warring, USA), polyethylene bottle, plastics, refrigerator, mortar, Ponar Graph sampler (Figure 3.8a), Horizontal water sampler (Figure 3.8b), Current Meter for measure, container, gloves, microwave digester (MILESTONE Ethos-E, Italy), ICPMS 7500a Agilent (Agilent Technologies, USA).



Figure 3.8. (a). Ponar Graph Sampler

(b). Horizontal water sampler

3.3.2 Reagent and Chemicals

Reagents may contain elemental impurities that might affect the integrity of analytical data. Owing to the high sensitivity of ICP-MS, high purity reagents should be used whenever possible. All acids used for this method must be of ultra high-purity grade. All the chemicals used have to be an analytical reagent grade. Ultra-pure water (18.2 M Ω) was used for all dilutions throughout the study. All plastic containers were cleaned by soaking in 10% (v/v) nitric acid for 24 h and rinsed with distilled water prior to use. HCl, HNO₃, H₂SO₄, H₂O₂ and HClO₄ were used for microwave digestion. Nitric acid is used for ICP-MS in order to minimize polyatomic ion interferences. Several polyatomic ion interferences is expected to occur when hydrochloric acid is used. For this case, corrections for the chloride polyatomic ion interferences must be applied to all data (USEPA, 1992).

In these methods, all acids of ultra high-purity grades were used. Concentrated $HNO_3 H_2SO_4$ and NH_4OH were purchased from Merck. $HNO_3 (1+1)$ was prepared to use deionised distilled water by diluting 500 mL concentrated HNO_3 acid to 1L and (1+9) NH_4OH was prepared by diluting 10 mL concentrated NH_4OH to 100 mL. Deionized distilled water (DDW) was used for preparation of solutions, dilutions and for final rinsing of the acid cleaned vessels.

3.4 Methods

3.4.1 Sampling Frequency

The field monitoring was carried out in the Balok River and Tunggak River begining in November 2010 until November 2012. Water and sediment samples were collected every month from six locations indicated in figure 3.1. The sampling areas were chosen based on assumptions possible sources of the heavy metal's pollution and also expected unpolluted areas along the Balok River and Tunggak River. All the sampling locations coordinate were recorded using a GPS (Global Position System) instrument. Process taking sample had done one times within 3 parts, namely the right side, the middle and the left edge of the grab sampler every site sampling, which is representative of the entire flow for the constituent of interest in the location study. All samples were collected and sent to the laboratory on the same day. Weather and physical conditions during sampling were recorded. Average flow rate of Balok and Tunggak River as category not high is around $0.9 - 1.20 \text{ m/s}^2$ was measurement by velocity meter on site sampling.

Chemical analyses were carried out in the Civil Environment laboratory and Faculty Industrial and Scientific Technology in the Universiti Malaysian Pahang, Gambang, Kuantan.

3.4.2 Parameter Measure

A total of 13 water quality parameters were tested either on site or through laboratory analysis, presented Table 3.2.

Parameters	Unit						
temperature	°C						
рН	Mg/L						
Dissolved Oxygen (DO)							
Chemical Parameters Organics							
Biochemical Oxygen Demand (BOD)	mg/L						
Chemical Oxygen Demand (COD)	mg/L						
Heavy Metals							
Aluminum	μg/L (ppm)						
Chromium	μg/L (ppm)						
Ferrum	μg/L (ppm)						
Nickel	μg/L (ppm)						
Copper	μg/L (ppm)						
Zinc	μg/L (ppm)						
Arsenic	μg/L (ppm)						
Cadmium	μg/L (ppm)						
Plumbum	μg/L (ppm)						
Mangan	μg/L (ppm)						

Table 3.2: List of parameters analyzed

3.4.3 Preparation of water samples

The water and sediment samples were collected during November 2010 until July 2011, when River Balok and Tunggak River had a high water level. The significant change of water quality in this area is not very clear because of the Balok River and Tunggak River includes Small River and is considered as shallow water (average depth 7-9m). In prior to water sample collection, the horizontal water sampler was rinsed with the sample solution. The water samples were collected manually from each sampling station and were of 50 cm beneath the surface. 2L capacity polyethylene bottles were used for storing the water that has been pre-cleaned and were preserved with ice packs during sampling duration before sent to the laboratory for analysis. In each location, triplicates of water sample were collected.

The water samples were then immediately acidified with (1+1) of HNO ultra high-purity grade 65% purchased from Merck to distilled water for maintained to a pH < 2 upon receipt in the laboratory. If the sample pH was above 1.85, (1+1) nitric acid was added to a drop wise manner, the sample was then mixed in the container by inverting and shaking it and the pH was predetermined. If the pH should go below 1.65, (1+9) ammonium hydroxide was added in a drop wise manner as the sample is within the pH range of 1.65 to 1.85. For the determination of acid-soluble metals, the pHadjusted sample is filtered through 0.45-µm membrane filter. Once the has filtration is completed, the filtrate was transferred to a labeled, cleaned polyethylene storage bottle and stored in a refrigerator at 4 C, until all analysis has been completed. The above procedure was repeated for all samples and these samples were used for ICP-MS analysis directly.

3.4.4 Preparation of sediment sample.

The sediment samples were collected at the same location of the water sample. At each station, triplicates of sediment sample were collected. The Ponar grabs sampler was used in this study in order to collect the sediment sample at about 20-40 cm deep from the river bed. The sediment sample was taken placed in a plastic bag and was preserved in the ice box before was taken to the laboratory for analysis. Upon arrival, the sediments were cleaned from twigs and pebbles. Later, they were subjected to the refrigerator at 4°C for further analysis. No chemical preservation was added to sediment sample. In prior to analysis the samples were dried at 80°C for 24 hours and were sieved through a polyethylene sieve of 200 µm in order to remove large particles as well as to

obtain homogenous sample. The samples were ground in to finer powder by an agate mortar for 30 minutes before passing through a nylon filter.

A 0.5 gr of well homogenized powder sediment samples was weight and transferred into Teflon digestion tube. They were leached by addition of a mixture of 3 ml HNO₃ 65% and 7 ml of HCL 37%. The round bottom flask was placed in a round shape heating mantle, and the solution was reflux at a temperature of 180°C for 30 minute. The digest was allowed to cool for 10 minute and then 2 ml of H₂O₂ were next slowly added drop wise to the digest until the effervescence stopped. The sediment was then sieved by using Whatman 41 filter paper for remove fine particles then filtrated transported to volumetric flask. The extracts (filtrated) were diluted to final volumes of 50 ml with deionized double distilled water (EPA, 2007). The sample has been ready for analysis using Inductivity Couple Plasma Mass Spectrometer (ICP-MS).

3.5 Analysis of heavy metal by ICP-MS

Mineral content of the sediment samples was determined by using being an Inductively Coupled Plasma – Mass Spectometer (ICP-MS) (Figure 3.3). Sediment and water were being analyzed for heavy metals (Al, Cr, Mn, Fe, Ni, Cu, Zn, As, Cd and Pb). A calibration curve was constructed using five concentrations (0-500 μ g/L) of standards prepared in-house. HNO₃ was used as a blank and all the analysis was performed in triplicates.

3.5.1 Sample preparation for mineral analysis

Sediment powders were prepared by accurately weighing approximately 0.5 g LP which was placed into a digestion vessel. HNO₃ solution (65%, 7 mL) and H₂O₂ (30%, 1 mL) were then added to each vessel. The vessels were then capped prior to placing into the rotor segment which in turn was inserted into the microwave cavity. The digester was operated at 200 °C and 1000 watt for 20 minutes after which the rotor was cooled. The vessel content was then emptied into a 50 mL volumetric flask. HNO₃ solution (2%) was added to the mark and the solution was mixed well.



Figure 3.9. Inductively Coupled Plasma Mass Spectroctroscopy (ICPMS) equipment

3.5.2 ICP-MS operating conditions

An Inductively Couple Plasma – Mass Spectrometer (ICPMS) was being used with the following operating conditions for determination of the minerals as being summarized in Table 3.10.



Figure 3.10 (a) Sample vessels and rotor (b) Microwave digester

Instrument		Agilent 7500a						
Nebulizer		Babington type						
Spray cham	ber	Scott-type						
Plasma								
RF generato	r	Frequency; 10 MH, Power output 1300 W						
Air flow rate	e (1/min)	Plasma; 15, auxiliary: 0.9, nebulizer: 1-1.1						
Sample upta	ke rate	1.8 ml/min						
Interface								
Samper cone	9	Nickel, id: 1.1 mm						
Skimmer		Nickel, id: 0.9 mm						
Vacuum		Interface: 4 torr, quadrupole: 2×10^{-5} torr						
Data acquisi	tion	Peak hoping, replicate time 200 ms, dwell time						
		200 ms, sweep reading 3, readings/replicate 3,						
		number of replicates 3						

Table 3.2 Operating conditions for ICP-MS

3.6 Analysis Statistic

Mean and standard deviation of water and sediment data, Enrichment Factor (EF), Contamination Factor (CF) and Pollution Load Index (PLI) were computed using Microsoft Excel 2007 version.

The interrelationships among elemental concentrations in water and sediment samples were analyzed by using Pearson's correlation methods of the SPSS version 16 software. Principal component analysis (PCA) and charts (line and bar graphs) for water and sediment data were performed by using SPSS version 16 software. As a conclusion the methodology of this study can be summarized in Fig.3.11.

Assessments of heavy metal deposition in water and sediment in Balok River and Tunggak River, Kuantan, Malaysia Selection of Monitoring Station Climate namely: Accessibility and ability to sample under all condition 1. 2. Homogeneity of the water column 3. The aquatic habitat present at the site The main tributaries combination the river 4. Location of the industrial areas, residential, and other activities human 5. Balok River Tunggak River Sampling In situ Laboratory Analysis 1. pН 2. Conductivity Water Sediment 3. velocity Microwave Digestion: 1. The sediment was accurately 0.5 gr weighed 2. Taken into Microwave Teflon vessel and acid mixture (7 ml HNO₃+ 3 ml H₂O₂) added shaken and homogenized and ensure the vessel are kept closed. The homogenized sediment was then subject to digestion for 3. 30 minute digestion in Microwave system (Microwave oven program) and later cooled to room temperature 4. The suspensions were filtered and the filtrates were collected in 50 mL flask. The filtrates were diluted with deinozed double-distilled water to 50 mL. Analysis heavy metal using ICP-MS Statistical analysis by using Pearson Correlation, ANOVA, PCA, EF, CF and PLI **Result and Discussions** END

Figure 3.11. Flow chart of the methodology

CHAPTER 4

RESULT AND DISCUSSION

4.1. Introductions

This chapter discusses the results obtained from the heavy metal test conducted on water and sediment sample of Balok River and Tunggak River by using ICP-MS.

In summary, the results of this study are presented and discussed as followings:

- 1. Heavy metal concentrations in water and sediment of three sampling points.
- 2. Correlation, ANOVA, PCA among heavy metal in water and sediment every site.
- Contamination Factor of heavy metals in water and sediment in Balok River and Tunggak River.
- 4. Pollution Load Index (PLI) of water and sediment at Balok River and Tunggak River
- 5. Enrichment Factor of heavy metal contamination level in sediment river system.

In this study, heavy metals such Al, Fe, As, Cu, Cd, Cr, Pb, Zn, Ni, and Mn, have been chosen as they are classified as principal pollutants and toxic for human beings.

4.2. Water Quality Parameters for Balok River

The physico-chemical parameters of the water column such as DO, pH, temperature, BOD and COD are important as they have a significant effect on the water

quality. The degradation f river water quality is detrimental to the healthy to the healthy aquatic life.

Thus, it is important in this study to determine these parameters at both rivers, that the physico-chemical parameters of a river have to be studied. Both in situ and laboratory testing were conducted in order to obtain the existing environmental information. The overall water quality results and the average water quality results at the six sampling points for the Balok River during November 2010 until November 2012 is presented in Table 4.1. The results were then compared to the DOE Interim National Water Quality Standards for Malaysia (INWQS). The INWQS can be refered to Appendix 17.

Station	pН	COD	BOD	DO	SS	AN
1	6.61±0.79	19.24±3.25	7.37±1.69	5.43±0.78	32.35±5.43	0.19±0.045
2	6.13±0.87	27.24±4.65	9.58±1.79	3.62±0.744	59.11±5.82	0.41±0.04
3	5.69±1.01	41.85±4.57	13.05±2.5	2.54±0.33	73.26±6.37	1.76±0.23

Table 4.1 Result of six water quality parameters

4.2.1 Chemical Oxygent Demand

The accountability of Chemical Oxigent Demand (COD) to the WQI is the third most important parameter when determining a river's WQI as it takes up 16% togheter with SS (DOE, 1986). In general gives an estimation of the amount of organic and inorganic matter present. Normally, the value of COD is higher than BOD. In this study the concentrations of COD observed for station 1, 2 and 3 of Balok River were 5.43 ppm, 27.24 ppm and 41.85 ppm respectively as in Figure 4.1. Based on the maximum recommended INWQS, threshold level COD for Malaysia Rivers is 100 ppm (Appendix A-17). The average values of COD for location 2 and 3 of the river systems were within the INWQS threshold level for class III except location 1 was class II. Therefore, the Balok River is safe for domestic water supply and irrigation only after future extra treatment.



Figure 4.1. The average chemical oxygent demand values for 3 sampling point along of the Balok River

4.2.2. Biological Oxygen Demand

Based on figure 4.2, it is found that the highest average reading of BOD was at location 3 with the reading of 13.05 ppm and it was INWQS threshold level for class III. Based on the results, it could be presumed that, at location 3 the BOD indicating the highest reading may due to that may probably increase the BOD reading at selected point. On the contrary, the lowest reading of BOD at location 1 with the reading of 7.37 ppm and location 2 was 9.58 ppm were within INWQS threshold level for class II. Thus, the water at the catchments area is doubt to be harmful and contaminated.



Figure 4.2. The average biological oxygent demand values for 3 sampling point along of the Balok River

4.2.3. Dissolved Oxygen

The average concentrations of DO for location 1, 2, and 3 at Balok River were 5.43 ppm, 3.62 ppm and 2.54 ppm, respectively, as shown in Figure 4.3. From the figure, the differences of DO concentration recorded during the study at different sampling site along Balok River can be seen. Location 1 and 2 of Balok Rivers showed DO values within the class II of INWQS thereshold level to support of aquatic life. While at location 1 theDO value was within the INWQS thereshold level for class III.



Figure 4.3. The average dissolved oxygen values for 3 sampling point along of the Balok River

4.2.4 Ammoniac Nitrogent

Figure 4.4 shows that the highest average reading of Ammoniac Nitrogen was 1.76 ppm and within class III of INWQS occurred at location 3 of Balok River. Meanwhile the lowest concentration average of AN was 0.19 ppm within the class II of INWQS occurred at location 1 of Balok River most likely due to its location which is located at the downstream of the catchments area and therefore less organic contaminants present. Meanwhile at location 2, the AN was 0.41 ppm and was within class II of INWQS.



Figure 4.4. The average Amoniac Nitrogen values for 3 sampling point along of the Balok River.

4.2.5 Suspended Solid

Based on the maximum recommended INWQS threshold level SS for Malaysia Rivers is >300 ppm (Appendix A-17). The average values of SS for location 1 (32.35 ppm) and 2 (59.11 ppm) of the river systems were within the INWQS threshold level for classes 1 except location 3 (73.26 ppm) presented on Figure 4.5. Therefore, the water of Balok River systems is safe for domestic water supply, irrigation after extra treatment.



Figure 4.5. The average Suspended Solid values for 3 sampling point along of the Balok River.

4.2.6 pH

Based on the result it clearly shows that the lowest average pH values was indicated on the location 3 with the average pH value of 5.69. Meanwhile, the highest average pH value was indicated at the location 1 with the average pH value of 6.61. Based on the results of pH in every sampling station at each sampling time, it shows that the changing pattern of pH value were moderately unvarying.



Figure 4.6. The average pH values for 3 sampling point along of the Balok River.

From the graph, it clearly shows that the average value results for pH at every sampling point were initially high at location1 because less contamination affecting to the water, and slightly drop at location 2 and location 3. The average pH at location 2 is 6.32, nearly neutral but less than 7 and indicates the water in acidic condition, because location 2 are located at downstream of catchments. For the location 1 near mouth of river and less human activity. Meanwhile, at location 3, the average value results for pH are decrease to 5.99 that indicates much acidic condition because low pH less than 5. This might be due to its location located exactly after the industrial area, whereby the direct discharged of wastewater to the catchments has affected the decreasing value of the water pH.

4.2.7. Water Quality Index (WQI)

The value of the water quality index (WQI) is determined by first obtaining the sub index value for each parameter. The WQI is good indicator of any deterioration or

improvment of a water body. Based on Table 4.2 and Figure 4.7. it shows that the sub index for WQI in station 1, 2, 3 of Balok River were 82, 74, and 61, respectively. Among the three staions, the WQI for station 1 is the highest. This is mainly due to its surrounding contain the lowest industrial activity while the remaining stations were surrounded with residential and industrial areas and other land use. From the value derived from the sub index, station 1 of Balok River is classified as Class II which is clean area. This is because surrounding of river systems has a lot of trees that can help to reduce river pollution. Meanwhile from the value derived from the sub index, location 2 and 3 is classified as Class II which is slight polluted.

Table. 4.2. Status of River Pollution on Water Quality Index (WQI) and Sub Index for Balok River

Station	SIpH	SIDO	SIBOD	SICOD	SISS	SIAN	WQI	Status
1	98	92	71	74	80	80	82	Clean
2	90	89	63	66	68	66	74	Slight Polluted
3	96	79	51	52	63	33	61	Slight Polluted



Figure 4.7 Water Quality Index of sampling site of Balok River performace

4.3. Heavy Metal concentrations in water and sediment in Balok River

The result of concentrations of 10 heavy metals (Al, Cr, Mn, Fe, Ni, Cu, Zn, As, Cd, and Pb) in location 1, 2 and 3 along Balok River water and sediment samples are reported in Appendix A1-A4.

For the water samples, the highest average Al concentration of 0.793 ppm was recorded at location 2, followed by location 1 at 0.734 ppm and the lowest at location 3 with concentration of 0.526 ppm. The maximum recommended of INWQS threshold level of aluminum for Malaysia Rivers is 0.5 ppm (Appendix A-17). In this study, the average values of aluminum for all sampling points of the river systems were not within the INWSQ for all class except location 3 as shown in Figure 4.8. The aluminum concentration found in this study exceeds the polluted level, therefore and it is not safe for human consumption but suitable for irrigation. Meanwhile the other heavy metals such as Cr, Mn, Cu, Cd and Pb concentrations in water sample of location 3 were the lowest compared to location 2 and location 1.

For sediment, the highest deposit of Al was found to be at location 3 with the concentrations of Al 10890.83 ppm. The average Al concentration in location 3 sediment was 10571.56 ppm. The reference location 1 sediment recorded Al concentration of 7448.51 ppm. A high level of detected shows that the sediments is polluted and could be due to the high discharged of effluent contained with aluminum from the massive industrial activities along the river bank such as electroplating, printing factor and also might be contributed by the occurrences of natural process.



Figure 4.8. Average aluminum values for 3 sampling points of the Balok River systems.

In this study, the presence of Cr in water samples for location 1, 2 and 3 were detected at concentrations 0.870 ppm, 0.190 ppm and 0.109 ppm were reported for location 1, 2 and 3, respectively. Based on the maximum recommended INWQS threshold level chromium for Malaysia Rivers is 0.1 ppm (Appendix A-17). The average values of chromium for location 1 and 2 of the river systems were not within the INWQS threshold level for all classes except location 3 (Figure 4.9). From this figure, it can be conducted that the water of Balok River is safe for domestic water supply and irrigation only after extra treatment is undertaken.

Meanwhile, the amount of Cr in location 1, 2 and 3 along Balok river sediments were 6.28 ppm, 12.60 ppm and 15.95 ppm, respectively. Generally, the present of Cr in sediment came from the chemical and metallurgical industry for the production of stainless steel and other alloys steels, and in the refractory. Hence, the water of Balok River systems is believed to be unsuitable for the supply of water for domestic, industrial and agricultural purposes as the concentrations of Cr detected is already above allowed limitations by INWQS. Furthermore, the Balok River could be classified as polluted and may risk the aquatic life of the river ecosystems.



Figure 4.9. Average chromium values for 3 sampling points of the Balok River systems.

In this study, the presence of Mn in water samples for location 1, 2 and 3 were detected at concentrations 0.18 ppm, 0.15 ppm and 0.17 ppm were reported for location 1, 2 and 3, respectively. Based on the maximum recommended INWQS threshold level Manganese for Malaysia Rivers is 0.2 ppm (Appendix A-17). The average values of chromium for location 1, 2 and 3 of the river systems were within the INWQS threshold level for classes IV (Figure 4.10). From this figure, it can be conducted that the water of Balok River is safe for domestic water supply and irrigation only after extra treatment is undertaken.

Meanwhile, the amount of Mn in location 1, 2 and 3 along Balok river sediments were 21.99 ppm, 24.15 ppm and 20.77 ppm, respectively. Generally, the present of Mn

in sediment came from the chemical and metallurgical industry for the production of stainless steel and other alloys steels, and in the refractory.



Figure 4.10. Average manganese values for 3 sampling points of the Balok River systems

Location 3 registered the highest Fe levels in both water and sediment samples. The average Fe concentration 6806.33 ppm in sediment samples of location 3 was the highest and location 1 was next with 5646.84 ppm whereas location 2 recorded the lowest of 5409.76 ppm. Average Fe level in water samples of location 3 was highest 411.700 ppm, followed by location 1 was 284.124 ppm and location 2 recording the lowest level of 196.943 ppm. The maximum recommended INWQS threshold level of Fe for Malaysian rivers is class IV mainly 5 ppm (Appendix A-17). The average values of all the sampling points of the river systems were out of the INWQS threshold level (Figure 4.11). In terms of ferrum, the river waters of Balok River systems were unsuitable for the support of aquatic life and supply water domestic, industrial, and agricultural uses for the above mentioned and sampling points except after extra

treatment. High level of ferrum in water Balok River may be from natural and anthropogenic sources but increasing of industry that uses heavy metal in the high amount can be an influence increasing of Fe in water river systems.



Figure 4.11. Average ferrum values for 3 sampling points of the Balok River systems

For the water samples, the highest average Ni concentration of 0.24 ppm was recorded at location 3, followed by location 2 at 0.15 ppm and the lowest at location 3 with concentration of 0.14 ppm. The maximum recommended of INWQS threshold level of Nickel for Malaysia Rivers is 0.9 ppm (Appendix A-17). In this study, the average values of Nickel for all sampling points of the river systems were within the INWSQ for class II (Figure 4.12). In terms of Ni, the river waters of Balok River systems were suitable for the supply of water for domestic, industrial and agricultural uses after treatment for the above mentioned sampling points

For sediment, the highest deposit of Ni was found to be at location 2 with the concentrations of Ni 2.97 ppm. The average Ni concentration in location 3 sediment



was 2.80 ppm. The reference location 1 sediment recorded Ni concentration of 2.08 ppm.

Figure 4.12. Average nickel values for 3 sampling points of the Balok River systems

In this study, the presence of Cu in water samples for location 1, 2 and 3 were detected at concentrations 0.15 ppm, 0.16 ppm and 0.17 ppm were reported for location 1, 2 and 3, respectively. Based on the maximum recommended INWQS threshold level Copper for Malaysia Rivers is 0.2 ppm (Appendix A-17). The average values of chromium for location 1, 2 and 3 of the river systems were within the INWQS threshold level for classes IV (Figure 4.13). From this figure, it can be conducted that the water of Balok River is safe for domestic water supply and irrigation only after extra treatment is undertaken.

Meanwhile, the amount of Cu in location 1, 2 and 3 along Balok river sediments were 2.19 ppm, 5.68 ppm and 5.23 ppm, respectively. All these sampling points are located at the Balok River which is a crowded industrial zone and there are many

chemical industries there. This show the major sources of Cu in the water body Balok River were probably contributed by the industries located at the upstream of the river. Water body Balok River that contains heavy metal flow to downstream and contaminates any location that flowed until to the mouth of the river.



Figure 4.13. Average copper values for 3 sampling points of the Balok River systems

In this study, the presence of Zn in water samples for location 1, 2 and 3 were detected at concentrations 2.34 ppm, 0.16 ppm and 0.727 ppm were reported for location 1, 2 and 3, respectively. Based on the maximum recommended INWQS threshold level Zinc for Malaysia Rivers is 0.4 ppm (Appendix A-17). The average values of Zinc for location 1, 2 and 3 of the river systems were within the INWQS threshold level for classes II (Figure 4.14). From this figure, it can be conducted that the water of Balok River is safe for domestic water supply, industrial and agricultural uses after treatment. Meanwhile, the amount of Zn in location 1, 2 and 3 along Balok river sediments were 6.50 ppm, 15.01 ppm and 13.27 ppm, respectively.



Figure 4.14. Average zinc values for 3 sampling points of the Balok River systems

In this study, the presence of As in water samples for location 1, 2 and 3 were detected at concentrations 0.13 ppm, 0.12 ppm and 0.29 ppm were reported for location 1, 2 and 3, respectively. Based on the maximum recommended INWQS threshold level As for Malaysia Rivers is 0.4 ppm (Appendix A-17). The average values of As for location 1, 2 and 3 of the river systems were within the INWQS threshold level for classes IV (Figure 4.15). From this figure, it can be conducted that the water of Balok River is safe for domestic water supply, industrial and agricultural uses after treatment. Meanwhile, the amount of As in location 1, 2 and 3 along Balok river sediments were 2.32 ppm, 2.04 ppm and 2.12 ppm, respectively.



Figure 4.15. Average arsenic values for 3 sampling points of the Balok River systems

In this study, the presence of Cd in water samples for location 1, 2 and 3 were detected at concentrations 0.02 ppm, 0.01 ppm and 0.05 ppm were reported for location 1, 2 and 3, respectively. Based on the maximum recommended INWQS threshold level Cadmium for Malaysia Rivers is 0.01 ppm (Appendix A-17). The average values of Cadmium for location 1, 2 and 3 of the river systems were not within the INWQS threshold level for all classes (Figure 4.16). The levels of Cd in the water of Balok River systems were not considered for human exposure otherwise after treatment due to Cd high toxicity for human. Meanwhile, the amount of Cd in location 1, 2 and 3 along Balok river sediments were 0.18 ppm, 0.15 ppm and 0.62 ppm, respectively.



Figure 4.16. Average cadmium values for 3 sampling points of the Balok River systems

In this study, the presence of Pb in water samples for location 1, 2 and 3 were detected at concentrations 0.59 ppm, 1.01 ppm and 0.81 ppm were reported for location 1, 2 and 3, respectively. Based on the maximum recommended INWQS threshold level Cadmium for Malaysia Rivers is 5 ppm (Appendix A-17). The average values of Cadmium for location 1, 2 and 3 of the river systems were not within the INWQS threshold level for classes IV (Figure 4.17). Meanwhile, the amount of Pb in location 1, 2 and 3 along Balok river sediments were 10.30 ppm, 7.98 ppm and 15.01 ppm, respectively.



Figure 4.17. Average plumbum values for 3 sampling points of the Balok River systems

All heavy metals concentrations in this study in the sediment at each sampling point were presented in Appendix A1 –A4. The trend of heavy metal concentrations in sediments from the Balok River for each of the sampling sites within seven times sampling is presented in Table 4.3. Meanwhile Table 4.4 listed the average concentrations of heavy metals in sediments for all the sampling. It can be summarized that the dominance of various heavy metals in the surface sediment of the Balok river as the following: Al>Fe>Mn>Cr>Zn>Pb>Cu>Ni>As>Cd. This indicates that aluminum is dominant and Cadmium is the less dominant found in sediments at all sampling points.

Table 4.3. Trend of heavy metals in sediment for the three samplings sites in Balok River during November 2010 – July 2011

Sampling site	Trend of heavy metal
Location 1	Al>Fe>Mn>Pb>Zn>Cn>As>Cu>Ni>Cd
Location 2	Al>Fe>Mn>Zn>Cr>Pb>Cu>Ni>As>Cd
Location 3	Al>Fe>Mn>Cr>Pb>Zn>Cu>Ni>As>Cd

Table	4.4.	Average	of	heavy	metals	concentration	in	sediment	(ppm)	for	the	three
		samplings	s sit	es in B	alok Riv	ver during Nov	em	ber 2010 –	Noven	nber	201	2

Elements	Al	Fe	Mn	Cr	Zn	Pb	Cu	Ni	As	Cd
Average (ppm)	9636.94	5954.31	22.31	11.61	11.60	11.09	4.89	2.62	2.20	0.32
Trend	Al>	Fe>	Mn>	Cr>	Zn>	Pb>	Cu>	Ni>	As>	Cd

All heavy metals concentrations in this study in the sediment at each sampling point were presented in Appendix A1 –A4. The trend of heavy metal concentrations in sediments from the Balok River for each of the sampling sites within seven times sampling is presented in Table 4.5. Meanwhile Table 4.6 listed the average concentrations of heavy metals in sediments for all the sampling. It can be summarized that the dominance of various heavy metals in the surface sediment of the Balok river as the following: Fe>Al>Zn>As>Cu>Mn>Cr>Pb>Cd>Ni. This indicates that Ferrum is dominant and Nickel is the less dominant found in sediments at all sampling points.

Table 4.5. Trend of heavy metals in water for the three samplings sites in Balok River during November 2010 – November 2012

Sampling site	Trend of heavy metal
Location 1	Fe>Zn>Al>Cr>Mn>Cu>As>Pb>Cd>Ni
Location 2	Fe>Zn>Al>As>Zn>Mn>Cr>Pb>Cd>Ni
Location 3	Fe>Al>Zn>Ni>Cu>Mn>Pb>Cr>As>Cd

 Table 4.6. Average of heavy metals concentration in water (ppm) for the three samplings sites in Balok River during November 2010 – November 2012

Elements	Fe	Zn	Al	Pb	Cr	Ni	Mn	Cu	As	Cd
Average (ppm)	212.95	2.31	1.65	0.80	0.45	0.19	0.17	0.16	0.14	0.03
Trend	Fe>	Al>	Zn>	As>	Cu>	Mn>	Cr>	Pb>	Cd>	Ni

From the explanations above it has proven that sediment has the ability to absorb heavy metal more than water. However, low concentration of metals in water might not be necessary reflected that the area was pollution free. The sediment might have accumulated metals from water column from time to time. Such situation could be observed from the high concentration of heavy metals in the sediment found in Balok River. The water level of Balok River influences by the South of China Sea that always enter and out every 6-12 hours per day.

4.4. Heavy metal concentrations in water and sediment of three sampling stations of Balok River.

Heavy metal concentrations in water and sediments of Balok River were determined at three sampling stations namely location 1 (downstream Nyior river), location 2 (sewage of residential and industry activities) and location 3 sewage of Industry Gebeng Area, for the study period (November 2010 until November 2012). ANOVA was used to compare the differences among them as depicted in Appendix A1-A4. The recorded values of the heavy metal concentrations in water and sediment samples are shown in Table A-5 to A-8 of Appendix A.

1. Aluminum

The distribution of aluminum concentrations in water and sediment at three sampling points is shown in Figure 4.18 and 4.19. The average of Al concentrations in water varied from 2.323 ± 0.168 ppm in location 1, 2.134 ± 1.153 ppm in location 2, and $1.228\pm0.0.626$ ppm in location 3 and average of Al concentrations in sediment varied from 7448.512±4128.416 ppm in location 1, while 10890.826 ± 6238.655 ppm in location 2 and 10571.557 ± 4996.562 ppm in location 3. When comparing of Al concentrations in three sampling point it was found that differences were not statistically significant (P>0.05) for water and sediment.

The average of Al concentrations in water varied in November 2010 to 1.011 ± 0.593 ppm, in March 2011 to 2.730 ± 1.537 ppm, in July 2011 to 4.033 ± 1.021 ppm, July 2012 to 0.730 ± 0.161 ppm, in September to 2012 1.370 ± 0.651 ppm, in October 2012 to 0.865 ± 0.158 ppm, and in November 2012 to 0.777 ± 0.024 ppm. Average of Al concentrations in sediment varied from 3813.616 ± 1112.337 ppm, in

March 2011 to 12722.362 ± 2741.176 ppm and July 2011to 12374.916 ± 2576.856 ppm. After comparing Al concentrations during 7 times in a year, it was found that the differences were statistically significant (P<0.05) for water and sediment.



Figure 4.18 Al concentrations in sediment of three sampling stations of Balok River during November 2010 until July 2011



Figure 4.19 Al concentrations in water of three sampling stations of Balok River during November 2010 until November 2012

2. Chromium

The distribution of Chromium concentrations in water and sediment at three sampling points is shown in Figure 4.20 and 4.21. The average of Cr concentrations in water varied from 0.978 ± 0.162 ppm in location 1, 0.246 ± 0.046 ppm in location 2, and 0.131 ± 0.094 ppm in location 3 and average of Cr concentrations in sediment varied from 6.278 ± 1.642 ppm in location 1, while 12.6 ± 3.485 ppm in location 2 and 15.949 ± 1.843 ppm in location 3. When comparing of Cr concentrations in three sampling point it was found that differences were not statistically significant (P>0.05) for water and were significant (P<0.05) for sediment.

The average of Cr concentrations in water varied in November 2010 to 0.031 ± 0.029 ppm, in March 2011 to 0.223 ± 0.199 ppm, in July 2011 to 0.200 ± 0.155 ppm, in July 2012 to 1.798 ± 0.274 ppm, September 2012 to 0.220 ± 0.181 ppm, in October 2012 to 0.257 ± 0.197 ppm, and November 2012 to 0.431 ± 0.053 ppm. Average

of Cr concentrations in sediment varied from 8.996 ± 4.662 ppm, in March 2011 to 13.109 ± 4.674 ppm and July 2011 to 12.722 ± 5.614 ppm. After comparing Cr concentrations during 7 times in a year, it was found that the differences were not significant (P>0.05) for sediment and water.



Figure 4.20 Cr concentrations in sediment of three sampling stations of Balok River during November 2010 until July 2011



Figure 4.21 Cr concentrations in water of three sampling stations of Balok River during November 2010 until November 2012

3. Manganese

The distribution of manganese concentrations in water and sediment at three sampling points is shown in Figure 4.22 and 4.23. The average of Mn concentrations in water varied from 0.177 ± 0.104 ppm in location 1, 0.145 ± 0.080 ppm in location 2, and 0.174 ± 0.085 ppm in location 3. Average of Mn concentrations in sediment varied from 21.996±7.444 ppm in location 1, while 24.152±15.623 ppm in location 2 and 20.774±8.309 ppm in location 3. When comparing of Mn concentrations in three sampling point it was found that differences were not significant (P>0.05) for water and sediment.

The average of Mn concentrations in water varied in November 2010 to 0.080 ± 0.035 ppm, in March 2011 to 0.210 ± 0.111 ppm, in July 2011 to 0.163 ± 0.011 ppm, in July 2012 to 0.292 ± 0.098 ppm, in September 2012 to 0.091 ± 0.016 ppm, in October 2012 to 0.218 ± 0.043 ppm and November 2012 to 0.103 ± 0.029 ppm. Average

of Mn concentrations in sediment varied from 10.524 ± 3.940 ppm, in March 2011 to 28.272 ± 6.214 ppm and July 2011to 28.125 ± 3.282 ppm. After, comparing of Mn concentrations during 7 times in a year, it was found that the differences were significant (P<0.05) for sediment and not significant (P>0.05) for water.



Figure 4.22 Mn concentrations in sediment of three sampling stations of Balok River during November 2010 until July 2011



Figure 4.23 Mn concentrations in water of three sampling stations of Balok River during November 2010 until November 2012

4. Ferrum

The distribution of ferrum concentrations in water and sediment at three sampling points is shown in Figure 4.24 and 4.25. The average of Fe concentrations in water varied from 183.444 ± 59.907 ppm in location 1, 171.695 ± 62.943 ppm in location 2, and 283.703 ± 187.780 ppm in location 3. Average of Fe concentrations in sediment varied from 5646.835 ± 2742.517 ppm in location 1, while 5409.763 ± 2748.980 ppm in location 2 and 6806.325 ± 2027.935 ppm in location 3. When comparing of Fe concentrations in three sampling point it was found that differences were not statistically significant (P>0.05) for water and sediment. The average of Fe concentrations in water varied in November 2010 to 232.207 ± 3.094 ppm, in March 2011 to 260.959 ± 142.923 ppm and in July 2011 to 200.871 ± 82.343 ppm, in July 2012 to 157.779 ± 5.684 ppm, in September to 260.875 ± 103.910 ppm.
Average Fe concentrations in sediment varied from 3212.918 ± 1152.663 ppm, in March 2011 to 7079.463 ± 922.650 ppm and July 2011 to 7570.542 ± 1263.442 mg/kg. After comparing Fe concentrations during 7 times in a year, it was found that the differences were statistically significant (P<0.05) for sediment and not significantly (P>0.05) for water.



Figure 4.24 Fe concentrations in sediment of three sampling stations of Balok River during November 2010 until July 2011



Figure 4.25 Fe concentrations in water of three sampling stations of Balok River during November 2010 until November 2012

5. Nickel

The distribution of nickel concentrations in water and sediment at three sampling points is shown in Figure 4.26 and 4.27. The average of Ni concentrations in water varied from 0.160 ± 0.032 ppm in location 1, 0.158 ± 0.098 ppm in location 2, and 0.258 ± 0.045 ppm in location 3 and average of Ni concentrations in sediment varied from 2.085 ± 0.550 ppm in location 1, while 2.973 ± 0.654 ppm in location 2 and 2.787 ± 0.207 ppm in location 3. When comparing of Ni concentrations in three sampling point it was found that differences were not statistically significant (P>0.05) for water and sediment.

The average of Ni concentrations in water varied in November 2010 to 0.029 ± 0.017 ml/L, in March 2011 to 0.041 ± 0.003 ml/L, in July 2011 to 0.043 ± 0.025 ml/L, in July 2012 to 0.130 ± 0.013 , in September 2012 to 0.075 ± 0.047 , in October 2012

to 0.192 ± 0.165 , and in November 2012 to 0.265 ± 0.045 . Average of Ni concentrations in sediment varied from 2.604 ± 1.017 ppm, in March 2011 to 2.788 ± 0.229 ppm and July 2011 to 2.453 ± 0.510 ppm. After comparing of Ni concentrations during 7 times in a year, it was found that the differences were statistically significant (P>0.05) for water and sediment.



Figure 4.26 Ni concentrations in sediment of three sampling stations of Balok River during November 2010 until July 2011



Figure 4.27 Ni concentrations in water of three sampling stations of Balok River during November 2010 until November 2012

6. Copper

The distribution of copper concentrations in water and sediment at three sampling points is shown in Figure 4.28 and 4.29. The average of Cu concentrations in water varied from 0.153 ± 0.031 ppm in location 1, 0.207 ± 0.065 ppm in location 2, and 0.129 ± 0.067 ppm in location 3 and average of Cu concentrations in sediment varied from 2.197±0.937 mg/kg in location 1, while 5.684 ± 3.418 ppm in location 2 and 5.231 ± 0.901 ppm in location 3. When comparing of Cu concentrations in three sampling point it was found that differences were not statistically significant (P>0.05) for water and sediment.

The average of Cu concentrations in water varied in November 2010 to 0.130 ± 0.068 ppm, in March 2011 to 0.171 ± 0.003 ppm, in July 2011 to 0.188 ± 0.085 ppm, in July 2012 to 0.130 ± 0.013 ppm, in September 2012 to 0.075 ± 0.027 ppm, in

October 2012 to 0.192 ± 0.065 ppm, and in November 2012 to 0.265 ± 0.045 ppm. Average of Cu concentrations in sediment varied from 2.683 ± 1.898 ppm, in March 2011 to 5.061 ± 2.440 ppm and July 2011 to 6.957 ± 3.358 ppm. After comparing of Cu concentrations during 7 times in a year, it was found that the differences were statistically significant (P>0.05) for water and sediment.



Figure 4.28 Cu concentrations in sediment of three sampling stations of Balok River during November 2010 until July 2011



Figure 4.29 Cu concentrations in water of three sampling stations of Balok River during November 2010 until November 2012

7. Zinc

The distribution of zinc concentrations in water and sediment at three sampling points is shown in Figure 4.30 and 4.31. The average of Zn concentrations in water varied from 2.902 ± 1.224 ppm in location 1, 1.903 ± 0.831 ppm in location 2, and 2.118 ± 0.743 ppm in location 3. Average of Zn concentrations in sediment varied from 6.502 ± 0.904 ppm in location 1, while 15.010 ± 5.230 ppm in location 2 and 13.270 ± 3.965 ppm in location 3. When comparing of Zn concentrations in three sampling point it was found that differences were not statistically significant (P>0.05) for water and were statistically significant (P<0.05) for sediment.

The average of Zn concentrations in water varied in November 2010 to 0.107 ± 0.030 ppm, in March 2011 to 1.913 ± 0.271 ppm, in July 2011 to 1.552 ± 1.045 ppm, in July 2012 to 2.504 ± 0.276 ppm, in September 2012 to 3.170 ± 0.445 ppm, in

October 2012 to 3.143 ± 1.471 ppm, and in November 2012 to 3.764 ± 1.471 ppm. Average of Zn concentrations in sediment varied in November 2010 to 8.304 ± 1.112 ppm, in March 2011 to 13.246 ± 5.416 ppm and July 2011 to 13.232 ± 7.042 ppm. After comparing of Zn concentrations during 7 times in a year, it was found that the differences were statistically significant (P<0.05) for water and sediment.



Figure 4.30 Zn concentrations in sediment of three sampling stations of Balok River during November 2010 until July 2011



Figure 4.31 Zn concentrations in water of three sampling stations of Balok River during November 2010 until November 2012

8. Arsenic

The distribution of arsenic concentrations in water and sediment at three sampling points is shown in Figure 4.32 and 4.33. The average of As concentrations in water varied from 0.127 ± 0.105 ppm in location 1, 0.117 ± 0.095 ppm in location 2, and 0.188 ± 0.057 ppm in location 3 and average of As concentrations in sediment varied from 2.321 ± 1.117 ppm in location 1, while 2.040 ± 1.233 ppm in location 2 and 2.116 ± 0.971 ppm in location 3. When comparing of As concentrations in three sampling point it was found that differences were not statistically significant (P>0.05) for water and sediment.

The average of As concentrations in water varied in November 2010 to 0.017 ± 0.005 ppm, in March 2011 to 0.238 ± 0.021 ppm and in July 2011 to 0.259 ± 0.083 ppm and average of As concentrations in sediment varied in November 2010 to

 0.920 ± 0.196 ppm, in March 2011 to 2.612 ± 0.421 ppm and July 2011 to 2.495 ± 0.150 ppm. After comparing of As concentrations during 7 times in a year, it was found that the differences were statistically (P<0.05) for sediment and not statistically significant (P>0.05) for water.



Figure 4.32 As concentrations in sediment of three sampling stations of Balok River during November 2010 until July 2011



Figure 4.33 As concentrations in water of three sampling stations of Balok River during November 2010 until November 2012

9. Cadmium

The distribution of cadmium concentrations in water and sediment at three sampling points is shown in Figure 4.34 and 4.35. The average of Cd concentrations in water varied from 0.022 ± 0.009 ppm in location 1, 0.014 ± 0.006 ppm in location 2, and 0.045 ± 0.107 ppm in location 3. Average of Cd concentrations in sediment varied from 0.184 ± 0.031 ppm in location 1, while 0.154 ± 0.096 mg/kg in location 2 and 0.616 ± 0.363 mg/kg in location 3. When comparing of Cd concentrations in three sampling point it was found that differences were not statistically significant (P>0.05) for water and sediment.

The average of Cd concentrations in water varied in November 2010 to 0.013 ± 0.008 ppm, in March 2011 to 0.136 ± 0.001 ppm, in July 2011 to 0.071 ± 0.039 ppm, in July 2012 to 0.061 ± 0.001 ppm, in September 2012 to 0.016 ± 0.007 ppm, in

October 2012 to 0.017 ± 0.009 ppm, in November 2012 to 0.027 ± 0.005 ppm. Average of Cd concentrations in sediment varied in November 2010 to 0.588 ± 0.291 ppm, in March 2011 to 0.155 ± 0.008 ppm and July 2011 to 0.212 ± 0.030 ppm. After comparing of Cd concentrations during 7 times in a year, it was found that the differences were not statistically significant (P>0.05) for water and sediment.



Figure 4.34 Cd concentrations in sediment of three sampling stations of Balok River during November 2010 until July 2011



Figure 4.35 Cd concentrations in water of three sampling stations of Balok River during November 2010 until November 2012

10. Plumbum

The distribution of plumbum concentrations in water and sediment at three sampling points is shown in Figure 4.36 and 4.37. The average of Pb concentrations in water varied from 0.591 ± 0.066 ppm in location 1, 1.009 ± 0.546 ppm in location 2, and 0.807 ± 0.036 ppm in location 3 and average of Pb concentrations in sediment varied from 10.301 ± 1.272 ppm in location 1, while 7.981 ± 5.108 ppm in location 2 and 15.012 ± 7.585 ppm in location 3. When comparing of Pb concentrations in three sampling point it was found that differences were not statistically significant (P>0.05) for water and sediment.

The average of Pb concentrations in water varied in November 2010 to 0.033 ± 0.010 ppm, in March 2011 to 0.229 ± 0.119 ppm, in July 2011 to 0.033 ± 0.015 ppm, in July 2012 to 1.347 ± 1.444 ppm, in September 2012 to 0.562 ± 0.545 ppm, in

October 2012 to 2.049 \pm 1.617 ppm and 1.364 \pm 0.747 ppm. Average of Pb concentrations in sediment varied in November 2010 to 6.464 \pm 3.958 ppm, in March 2011 to 13.172 \pm 2.299 ppm and July 2011 to 13.634 \pm 7.327 ppm. After comparing of Pb concentrations during 7 times in a year, it was found that the differences were not statistically significant (P>0.05) for sediment and were statistically significant (P<0.05) for water.



Figure 4.36 Pb concentrations in sediment of three sampling stations of Balok River during November 2010 until July 2011



Figure 4.37 Pb concentrations in water of three sampling stations of Balok River during November 2010 until November 2012

The Balok River carriers natural and anthropogenic pollutants, mainly heavy metal concentration of Al, Cr, Mn, Fe, Ni, Cu, Zn, As, Cd and Pb which are released from small-medium industrial effluents, market, domestic waste water, leaching bedrock, etc. When comparing Cr, Mn, Fe, Ni, As, Cd and Pb concentrations in water at three sampling stations in Balok River, it was found that elements were not statistical significant (P>0.05) except Al, Cu and Zn were statistical significantly different between sampling point in Balok river. When comparing Al, Cr, Fe, Ni, Cu, Zn, Cd, and Pb concentrations in sediment at three sampling stations in Balok river it was found that elements were not statistical significant (P<0.05) except Al, Cu and Zn were statistical significantly different between sampling point in Balok river. When comparing Al, Cr, Fe, Ni, Cu, Zn, Cd, and Pb concentrations in sediment at three sampling stations in Balok river it was found that elements were not statistical significant (P<0.05) except Mn and As were not statistical significant different between sampling point in Balok river.

These are probably natural sources, anthropogenic and topography of river that influence the environment. Zhang *et al.*, 2009 revealed that concentrations of Pb and Cu in water have no correlation with those in soil due to the persistently flow of water.

Gonzalez *et al.*, 2010 revealed that accumulation of heavy metals takes place greatly in marine sediments, especially in proximity to anthropogenic sources (inner part of the bay and harbors), however pollution can be spread to a greater depth, and eventually affecting the whole ecosystem. Sediment generally possesses the high ability to absorb metal's releases from pollution sources (Hang *et al.*, 2009; Nvodic *et al.*, 2006). Moreover, the correlation coefficients of total heavy metals suggest that discharged wastewater from the plant not only enhance the concentration of heavy metals, but also influence the topography of the river and the depth of the river because the difference in the depth might result in the migration of polluted sediment from upstream to downstream (Hang *et al.*, 2009).

The Balok River has been previously to contain a high concentration of Aluminum in its water column at all sampling sites which then could be introducing a significant quantity of this metal on all sediments of the sites. It is important to mention that total aluminum concentrations in these sediments do not present a significant seasonal variation as observed in Figure 4.8, but depended on the human activity at the surroundings. In fact, there are some industrial activities, especially chemical industry, metal manufacturing, and residential located near Balok river that could increase the level of Al to the aquatic systems, as well as other metallic contaminants like Fe, Cr, Ni, Mn, Cu, Cd, As, Pb, etc., by discharging their untreated/or treated wastes directly to the Balok River. Therefore, it is not surprising as well with the present of concentrations of Al, Cr, Mn, Fe, Ni, Cu, Zn, As, Cd and Pb in water and sediment found in the study within a limit alarming and must give more attention for prevent bad impact on human welfare.

There are many chemical industries like Caltex, MTBE, BASF Petronas Chemical, Kanekan Malaysia, etc., vegetable refinery Cargil, poliplastic industry and transport companies such as Lee Thong Hung Trading and Transportations Sdn Bhd, and Institute Latihan Perindustrian Kuantan (ILPKN) near Balok River. This is indicated that commonly all of companies contain less of Cd as primary material in process production. Otherwise, the cadmium concentration in sediment samples was the lowest but still needed to give more attention due to Cadmium very toxic to human life otherwise in low concentration.

Ghrefat *et al.*, 2010 study about concentrations of Cd in Kafrain Dam then obtained Cd concentrations was lower than that of Pulicat Lake, India (Kamala-Kannan *et al.*, 2007) and the Seyhan Dam (Cevik *et al.* 2009). It is believed that water circulation in the river may affect the heavy-metal accumulation in both water and sediments. In this study, concentrations of heavy metal accumulated in sediment was higher than accumulated in water due to water impoundment for longer periods, site specific activities and the flow rate of river. Allan *et al.*, 2006mentioned that Characteristics of water are continually changing (e.g. water renewal, dilution process, etc.) and usually contain very low concentrations of contaminants (sometimes below detection limits) making identification of pollution events a difficult task.

Nevertheless, sediments are known to act as sink and reservoir for wide-range pollutants, including heavy metals (Morrillo *et al.*, 2007), reaching higher concentrations than in the water column, which makes measurement easier. Therefore, the result of the present study showed that the heavy metal concentrations accumulate in sediments can represent the activities available in the area and are likely to increase with growing industrial, agricultural, population, and, etc.

4.5. Relationship element in Location 1

The downstream of Nyior River has received untreated/treatment wastewater from the where small-medium industries, wet markets and established residents located. The Pearson correlation coefficients of the heavy metals in water and sediment samples at this location 1 are depicted in Table 4.7 below.

А.	Al	Cr	Mn	Fe	Ni	Cu	Zn	As	Cd	Pb
Al	1									
Cr	0.630**	· 1								
Mn	0.598	0.220	1							
Fe	0.743**	· 0.503	0.885*	1						
Ni	0.467	0.590	0.589	0.702*	1					
Cu	0.782	0.535*	0.393	0.634	0.117	1				
Zn	-0.016	0.131	0.054	0.009	0.663	-	1			
	0.640	0 501	0.010	0.620.4	0.011	0.408	0.450			
As	0.649	0.581	0.319	0.629*	0.011	0.386	-0.452	1	1	
Cđ	-0.618	-0.523	0.315	-0.160	0.218	-0.57	0.232	-0.217	1	4
Pb	0.064	0.485	-0.120	-0.144	0.439	0.010	0.541	-0.144	-0.140	I
В.	Al	Cr	Mn	Fe	Ni	Cu	Zn	As	Cd	Pb
Al	1									
Cr	0.743**	· 1								
Mn	0.279	0.005	1							
Fe	0.689*	-0.173	0.562	1						
Ni	0.854*	0.339	0.309	-0.006	1					
Cu	-0.297	0.745*	-0.056	-0.04	-0.062	1				
Zn	0.258	-0.228	0.512*	-0.071	0.102	-0.015	1			
As	0.356	0.294	0.572**	-0.031	0.318	- 0.065	0.247	1		
Cd	0.334	-0.075	0.516*	0.146	-0.161	0.095	0.451	0.505*	1	
Pb	-0.281	0.042	0.319	-0.327	0.435	0.057	0.263	0.077	-0.05	1
*. Co	rrelation	is significa	nt at the 0	.05 level ((2-tailed)	•				
**. C	orrelatio	ı is signific	ant at the	0.01 level	(2-tailed	l).				
$\mathbf{A} : \mathbf{S} \mathbf{e}$ $\mathbf{R} \cdot \mathbf{W}$	ediment s Vater som	ample ple	1							
D. W	D. Water sample									

 Table 4.7. Correlation matrix of level of heavy metals in riverine sediment and water

 samples location 1 Balok River

From Table 4.7, there are strong positive correlation coefficients between the elements in river sediments and the correlation between elements in the sediments sample is shown in Table 4.8 Meanwhile in Table 4.9, it shows the correlation between elements in the water sample.

Pairs of elements	Coefficients		
Al-As	0.692*		
Cr-Zn	0.793*		
Mn-Zn	0.722*		
Fe-Cu	0.711*		
Zn-As	0.685*		
Zn-Cd	0.749		
Zn-Pb	0.872		

Table 4.8. Pairs of correlation element in sediment sample

*. Correlation is significant at the 0.05 level (2-tailed). **. Correlation is significant at the 0.01 level (2-tailed).

Elements in river water samples showed strong positive correlation coefficients between themselves as follows Table 4.9.

Pairs of elements	Coefficients
Al-Cr	0.743**
Al-Ni	0.854*
Al-Fe	0.689*
Cr-Cu	0.745*
Mn-Fe	0.562*
Mn-Zn	0.512*
Mn-As	0.572**
Mn-Cd	0.516*
As-Cd	0.505*

Table 4.9. Pairs of correlation element in water sample

*. Correlation is significant at the 0.05 level (2-tailed).

**. Correlation is significant at the 0.01 level (2-tailed).

From Table 4.8 and Table 4.9, it is clearly shows that these metals are associated with each other, and the relationship does exist between the variables. It is indicates that metals in water and sediment in location 1 of Balok River have same sources pollution from anthropogenic. This is due to at the upstream of location 1, there are so many

human activities such as residential, wet market, traffic highway and small industry that always produce wastewater every day and discharge to Nyior River.

Gherefat *et al.*, 2010 revealed positive correlated with each other metal at the 99% confidence level, which suggested a common pollution source or same geochemical behavior for these metals. According to Zabetoglou *et al.*, (2002), Fe and Mn oxides/hydroxides have a high affinity with most trace metals and Fe often correlate with concentrations of other metals in aquatic environments.

E	lement	Correlat	tion Coefficients
	Al		0.825*
	Cr		0.603*
	Mn		0.428
	Fe		-0.722*
	Ni		0.853*
	Cu		0.661*
	Zn		0.420
	As		0.749
	Cd	/	-0.256
	Pb	ЯE	0.229
 a	1	1 10	1 0 0 7 1 1 10 11

Table 4.10. Pearson's correlation element in water-sediment in location 1

*. Correlation is significant at the 0.05 level (2-tailed).

**. Correlation is significant at the 0.01 level (2-tailed).

Al and Ni concentrations between the water and sediment show a positively significant correlation while Ni concentration shows the highest significant correlation with coefficient value of 0.853 at the 0.01 level (Table 4.10), while Fe that showed negatively correlations. There is no positive significant correlation for Mn, Zn, As, and Pb concentration and no negative significant correlation for Cd. The positive correlation suggested the same direction of accumulation and vice versa for the negative correlation.

Therefore, Al and Cr concentration in the water increase while those in sediments also increase. On contrary, Fe concentration in water increases while those in sediment decrease. In the case of Mn, Zn, As, Pb, and Cd, the relation between accumulated in water and sediment cannot be established. The lack of correlation for distribution of most heavy metals between the water body and sediment may be due to the constant water following into the Balok River. Zhang *et al.*, 2010 furthermore revealed the correlation of metals between water, and soils are weak according to Pearson's correlation analysis. This is mainly due to the high-flow rate of the Pearl River estuarine wetland.

Sediment analysis is more helpful to detect pollution problems and sources, particularly for contaminants that are rapidly absorbed by particulate matter and consequently, would not remain in water samples for long. When river flow is the low, particulate matter suspended in the water settles to the riverbed and is incorporated into the sediment. Factors such as water flow (especially after a high discharge), and particle size has to be taken into account, when sediments are used to assessment and monitor metal pollution in the rivers. For example, a lower degree of contamination would be calculated after a high discharge due to erosion of the river bed sediments (Forstner 1980).

4.6. Relationship element in Location 2

The result show that municipal and domestic discharges to the river from the populated urban area contained high concentrations of heavy metals. The Pearson correlation coefficients of the heavy metals in water and sediment are summarized in Table 4.11 below.

А.	Al	Cr	Mn	Fe	Ni	Cu	Zn	As	Cd	Pb
Al	1									
Cr	0.728*	1								
Mn	0.957**	0.769*	1							
Fe	0.923**	0.634	0.895**	* 1						
Ni	-0.309	-0.400	-0.335	-0.444	1					
Cu	0.784*	0.599	0.728*	0.739*	-0.309	1				
Zn	0.651	0.275	0.645	0.432	-0.143	0.346	1			
As	0.664	0.411	0.599	0.728*	-0.429	0.910**	0.228	1		
Cd	0.433	0.507	0.385	0.390	-0.204	0.643	0.024	0.734*	1	
Pb	0.953**	0.759*	0.972**	* 0.832**	-0.166	0.665	0.685*	0.511	0.407	1
D	A 1	Cr	Mn	Ea	NG	Cu	7n	Ac	Cd	Dh
B .	AI	Cr	IVIII	ге	INI	Cu	ZII	As	Cu	PD
AI	1									
Cr	0.803*	1								
Mn	0.430	0.882	1							
Fe	-0.621**	-0.342	0.029	1						
Ni	0.533*	0.601*	-0.415	-0.539	1					
Cu	0.400	0.027	0.552*	0.092	-0.112	1				
Zn	0.733*	0.513**	0.903*	0.542*	0.689	0.209	1			
As	0.649**	0.522*	0.008	-0.540	0.447	0.195	0.201	1		
Cd	0.677**	0.617**	0.429	-0.387	0.511	0.107	0.726*	0.511**	1	
Pb	0.762**	0.806*	0.103	-0.699	0.277	0.681	0.529	0.600**	0.593*	1
*. C	*. Correlation is significant at the 0.05 level (2-tailed).									

Table 4.11. Correlation matrix of level of heavy metals in riverine sediment and water samples location 2 Balok River

**. Correlation is significant at the 0.01 level (2-tailed).

The correlation analysis was conducted between heavy metal concentrations in sediment samples in order to assess the possibility of the similar origin of the metals. There are strong positive correlation coefficients between the elements in river sediments as shown Table 4.12.

A : Sediment sample

B: Water sample

Pairs of elements	Coefficients
Al-Cr	0.728*
Al-Mn	0.957**
Al-Fe	0.923**
Al-Cu	0.784*
Al-Pb	0.953**
Cr-Mn	0.769*
Cr-Pb	0.759*
Mn-Pb	0.972**
Fe-Cu	0.739*
Fe-As	0.728*
Fe-Pb	0.832*
Cu-As	0.910**
Zn-Pb	0.685*
As-Cd	0.734*

Table 4.12. Pairs of correlation element in sediment sample

*. Correlation is significant at the 0.05 level (2-tailed). **. Correlation is significant at the 0.01 level (2-tailed).

From the table 4.12, the heavy metals are considered has the same origin if the connection showed a positive correlation (Salati and Moree, 2010). Meanwhile from Table 4.13 elements in river samples showed strong positive and negative correlation coefficients between themselves.

	Pairs of elements	Coefficients
	Al-Cr	0.803*
	Al-Fe	-0.621**
	Al-Ni	0.533*
	Al-Zn	0.733*
	Al-As	0.649**
-	Al-Cd	0.677**
	Al-Pb	0.762**
	Cr-Zn	0.513**
	Cr-As	0.522*
	Cr-Cd	0.617**
	Cr-Pb	0.806*
	Mn-Cu	0.552*
	Mn-Zn	0.903*
	Fe-Zn	0.542*
	Zn-Cd	0.726*
	As-Cd	0.511**
	As-Pb	0.600**
	Cd-Pb	0.593**

Table 4.13. Pairs of correlation element in water sample

*. Correlation is significant at the 0.05 level (2-tailed).

**. Correlation is significant at the 0.01 level (2-tailed).

It is clearly show that Al dominated correlation with Cr, Fe, Ni, Zn, As, Cd and Pb in water. It is therefore suggested a common pollution origin for these elements as well as having geochemical behaviors. Liu *et al.*, 2011 in their study revealed the strong positive correlation between V, Cr, Co, Ni, Cu, Zn, and Fe each other in sediment samples of the Pearl River Estuary indicates that these metals might have similar origin. In general, negative and inverse correlations between metals indicate that these metals are derived from different sources or origins these metals are not associated with other metals (Ghreafet *et al.*, 2010).

Element	Correlation Coefficients		
Al	0.911**		
Cr	0.590		
Mn	0.211		
Fe	-0.704**		
Ni	0.113		
Cu	0.855		
Zn	0.443		
As	0.701**		
Cd	0.619		
Pb	0.602*		

Table 4.14. Pearsons' correlation of element in water-sediment location 2

*. Correlation is significant at the 0.05 level (2-tailed). **. Correlation is significant at the 0.01 level (2-tailed).

From Table 4.14 it is shows that Al, As and Pb concentrations between the water and sediment depicted a positively significant correlation with Al concentration shows the highest significant correlation with coefficient value of 0.911 at the 0.01 level, and Fe showed a negative correlations with coefficient value of -0.704 at the 0.01 level. Meanwhile there is no positive significant correlation for Cr, Mn, Ni, Cu, Zn and Cd concentration. The positive correlation suggested the same direction of accumulation and vice versa for the negative correlation. Therefore, as the one of Al, As and Pb concentration in the water increase the concentration those element in sediments also increase. On contrary, Fe concentration sediment decreases although its concentration iin water increases. In case of Mn, Ni, Cu, Zn, As, Pb, and Cd, the relation between accumulation in water and sediment could not be established.

4.7. Relationship element in Location 3

Condition of environment in this area very influenced by activity industry due to near with big chemical factory that always discharged untreatment/treatment wastewater to Balok River. Therefore, inter correlation between heavy-metal accumulation in

water and sediment needs to know for identification common for a pollutant. Table 4.15 depicted result correlation heavy metal in location 3.

A.	Al	Cr	Mn	Fe	Ni	Cu	Zn	As	Cd	Pb
Al	1									
Cr	0.475	1								
Mn	0.457	0.767*	1							
Fe	0.651	0.367	0.587	1						
Ni	0.055	0.560	0.396	-0.364	1					
Cu	0.684*	0.727*	0.630	0.562	0.463	1				
Zn	0.453	0.621	0.776*	0.414	0.539	0.630	1			
As	-0.558*	0.297	0.523	0.159	0.598	0.551	0.722*	1		
Cd	-0.834**	-0.528	-0.610	-0.485	-0.231	-0.562	-0.404	-0.608	1	
Pb	0.797*	0.549	0.517	0.449	0.476	0.893**	0.654	0.719*	-0.661	1
D	A 1	Cr	Ma	Ea	NI:	Cu	7.	10	Cł	- Dh
В.	Al	Cr	Min	Fe	INI	Cu	Zn	As	Ca	PD
Al	1									
Cr	0.802*	1								
Mn	0.414	0.639	1							
Fe	-0.643**	-0.649	0.003	1						
N1	0.884*	0.501	-0.015	-0.662	1					
Cu	0.488	0.539	0.707*	0.072	-0.104	1				
Zn	0.521*	0.868**	0.674*	-0.331	0.585	0.689*	1			
As	0.702	0.787*	0.179	-0.612*	0.521	0.912*	0.625*	1		
Cd	0.829**	0.801**	0.177	-0.824**	0.625	0.127	0.701	0.778**	1	
Pb	0.301	0.776*	0.785*	-0.455	0.387	0.588	0.523*	0.883**	0.781*	1
*. Co	*. Correlation is significant at the 0.05 level (2-tailed).									

Table 4.15. Correlation matrix of level of heavy metals in riverine sediment and water samples location 3 Balok River

**. Correlation is significant at the 0.01 level (2-tailed).

A : Sediment sample B : Water sample

There are strong positive and negative correlation coefficients between the elements in river sediments as shown in Table 4.16.

Pairs of elements	Coefficients		
Al-Cu	0.684*		
Al-Pb	0.797*		
Cr-Mn	0.767*		
Cr-Cu	0.727*		
Mn-Zn	0.776*		
Cu-Pb	0.893**		
As-Pb	0.719*		
Al-Cd	-0.834*		
Al-As	-0.558**		

Table 4.16. Pairs of correlation element in sediment sample

*. Correlation is significant at the 0.05 level (2-tailed).

**. Correlation is significant at the 0.01 level (2-tailed).

Table 4.17 elements in river water samples showed strong negative correlation coefficients between themselves. It is shows clearly that Al was significantly positively and negatively correlation with all the measured heavy metals, implying that there are some sources of Al that are currently unknown. Especially, Al, Cu, and Pb were generally highly correlated each other, these indicating that the general contamination sources for these metals (Manta *et al.*, 2002; Al-Kashman and Shawabkeh 2006) were primarily traffic and industrial activity. For Al-Cd (-0.892) and Al-Ni (0.884) were concentrations showed a strong negative correlation at 0.01 level (2-tailed). Negative and inverse correlations between metals indicate that these metals are derived from different sources and that this metal is not associated with other metals (Ghreafet *et al.*, 2010).

Pairs of elements	Coefficients
Al-Cr	0.802**
Al-Fe	0.643*
Al-Ni	0.884*
Al-Zn	0.521*
Al-Cd	0.892**
Zn-Cr	0.868**
As-Cr	-0.778*
Cd-Cr	0.801**
Pb-Cr	0.766*
Cu-Mn	0.707*
Zn-Mn	0.674*
Pb-Mn	0.785*
Zn-Fe	-0.670*
Cu-Zn	0.689**
Cu-As	0.912*
Zn-Pb	0.523*
As-Cd	0.778*
As-Pb	0.883**
Cd-Pb	0.781*

Table 4.17. Pairs of correlation element in water sample

*. Correlation is significant at the 0.05 level (2-tailed). **. Correlation is significant at the 0.01 level (2-tailed).

It should be noted that Pb was a high significantly positively correlation with all the measured heavy metals, indicating that it may be the influence by anthropogenic activity in this area. Present of Pb, Cd and Zn are probably the result of anthropogenic activities mainly include the effluent of wastewater treatment plants, treated and untreated wastewater, agricultural, residential and irrigation return water (Ghreafet *et al.*, 2010, Boruvka *et al.*, 2005).

Element	Correlation Coefficients
Al	0.452
Cr	0.661*
Mn	0.267
Fe	-0.391
Ni	0.877
Cu	0.331
Zn	0.854
As	0.672*
Cd	-0.445
Pb	0.896**

Table 4.18. Pearson's correlation element in water-sediment location 3

*. Correlation is significant at the 0.05 level (2-tailed). **. Correlation is significant at the 0.01 level (2-tailed).

From Table 4.18 it is show that Cr, As and Pb concentrations between the water and sediment show a positive significant correlation while Pb concentration shows the highest significant correlation with coefficient value of 0.896 at the 0.01 level. There is no longer the positive significant correlation Al, Mn, Ni, Cu, Zn, and Pb concentration and there is no negative significant correlation Fe and Cd. The result shown that weak correlation between water and sediment, due to the constantly flow of water that always changed every time.

4.8. Principal Component Analysis (PCA) on sediment in location 1

Principal component analysis has been carried out on the raw data of total heavy metals accumulated in sediment. Factors with Eigenvalues greater than 1 were taken into account. Two principal components (PCs) were extracted, together, explained 67.104% of the total variance in sediment dataset. Variable loading coefficients of the two principal components are listed in Table 4.19. The graphic represented on the two

components is also shown in Figure 4.38. From this figure, it is believed that the sources of the pollution possibly from anthropogenic and natural origins.

Table	4.19.	Matrix	of the	principal	component	analysis	loading	of	metals	and	major
		element	s of riv	er sedime	nt in Balok I	River. ^{a,b}					

Heavy Metal		Component		
		PC1	PC2	
Al	/	0.961		
Fe		0.876		
Cr		0.819	0.218	
Cu		0.798	-0.336	
As		0.647	-0.412	
Mn		0.639	0.229	
Zn			0.925	
Ni		0.539	0.806	
Pb			0.633	
Cd		-0.347	0.398	
Eigenvalue		4. 2673	2.4430	
% of Total Variance		42.673	24.430	
Cumulative%	of variance	42.673	67.104	

^a Extraction Method: Principal Component Analysis; Rotation Method: Varimax with Kaisar Normalization.; Rotation converged in 5 iterations. ^b The boldfaced numbers are the dominant elements in different PCs

The first principal component (PC1) has the highest Eigenvalue of 4.267%, accounting for 42.673% of the total variance was strong positively correlated with Al, Fe, Cr, Cu, As, Mn, and Ni, which registered 0.961, 0.876, 0.819, 0.798, 0.647, 0.639 and 0.539 respectively. This component can be termed "natural factor" because the concentrations of heavy metals seem to be controlled by parent rock composition.

Component Plot in Rotated Space



Figure 4.38 Plot of loading PCA location 1 sediment in Balok River

Meanwhile The second principal component (PC2) shows of 24.430% of the total variance with an eigenvalues 2.443% the total variance and was strong positively correlated with Zn, Ni, and Pb. Therefore, this component could be identified as "anthropogenic factor" because of its high level presence in sediment. In general, the strong relationship among Ni, Pb and Zn elements may reflect an anthropogenic contamination of urban soils, particularly from vehicle emissions (Lie *et al.*, 2004). Veldes *et al.*, 2010 in their study believed that gasoline combustion rubber tire wear, auto-workshop, electroplating industries, as well as domestic wastewater are probably the major sources of Pb, Cr, Zn, and Cd. Meanwhile, for Ni which is also presented in PC1 was primarily due to of the natural process from the parent rock but due to anthropogenic activities in this area (industry and residential) causes mobility of Ni increasing.

In location 1 (downstream Nyior River), less human activity due to dominate with forest, but on the upstream Nyior River there are many residential established that always discharge domestic waste to river system. Present of Pb, Zn, and Ni probably were attributed to anthropogenic inputs such as vehicle traffic across the causeway, domestic waste, market, and small industry that discharges wastewater to Nyior river that contained the heavy metal flow until downstream (location 1) as channel to contact to Balok River.

4.9. Principal Component Analysis (PCA) on water in location 1

Principal component analysis has been carried out on the raw data (Appendix A3) of total heavy metals accumulated in water. Factors with eigenvalues greater than 1 were taken into account. Three principal components (PCs) were extracted, together, explaining 87.689% of the total variance in water dataset. Variable loading coefficients of the three principal components are listed in Table 4.20. The graphic to represent on the three components is also shown in Figure 4.39. These factors are possibly anthropogenic and natural origins.

Heavy Meta	al	Compone	nt	
		PC1	PC2	PC3
Zn		0.844	-0.23	5 -0.114
Pb		0.539	-0.24	9
Mn		0.848		
Cr		0.642		0.229
As		0.709	0.450	0.259
Cd		0.729	0.431	-0.305
Al		0.710	-0.42	9 0.413
Cu			0.955	
Fe			0.872	-0.247
Ni		0.128	-0.10	6 0.901
Eigenvalue		7.002	1.125	0.641
% of Total Va	riance	70.024	11.25	6.413
Cumulative% of	of variance	70.024	81.27	6 87.689

Table 4.20. Matrix of the principal component analysis loading of metals and major elements of river water in location 1 Balok River. ^{a,b}

^a Extraction Method: Principal Component Analysis; Rotation Method: Varimax with Kaisar Normalization.; Rotation converged in 4 iterations.

^bThe boldfaced numbers are the dominant elements in different PCs

Component Plot in Rotated Space



Figure 4.39. Plot of loading PCA location 1 water in Balok River

The first PC, accounting for 70.024% of the total variance with an eigenvalues of 7.002% was positive correlated with Zn, Pb, Mn, Cr, As, Cd, and Al, with the absolute factor loading recorded absolute factor loading greater than 0.5 were 0.844, 0.539, 0.848, 0.642, 0.709, 0.729 and 0.710 respectively. This component can be termed "anthropogenic factor" due to Zn, Pb, Cr, As, and Cd related to human activity otherwise Al and Mn are lithogenic elements. The higher load of Zn, Pb, Mn, Cr, As, Cd may be attributed to the composite waste of municipal and industrial effluents, especially from market, and small industry (home industry) and vehicle repair shop which utilize these metals in their process production. Water more sensitive to the contamination pollutants compared sediment, but water cannot be sinking of the pollutant due to flow rate of river water and water easy for response change of environment.

The second PC, explained 11.252%, of the total variance with an eigenvalues 1.125% and dominated by Cu and Fe recorded absolute factor loading greater than 0.5. The lithogenic factor dominates that distribution of most part of the considered elements in this study. Khrisna *et al.*, 2009 reported that Fe and Ni exhibit natural background concentrations in groundwater. Cu also origin anthropogenic activity due to same component with Fe, therefore, Cu shows migrative characteristic in the water sample.

However, Cu may be related with slurry application, this indicating a mixed origin lithogenic and anthropogenic (Uria *et al.*, 2009).

The third PC, accounting for 0.641% of the total variance with an eigenvalues 6.413%, was weighted only Ni. Ni was univocally isolated in the third component (PC3) of the water samples Balok river and showed a weak associated with other elements, which may indicate that it had some unique sources.

4.10 Principal Component Analysis (PCA) on sediment in location 2

Principal component analysis has been carried out on the raw data (Appendix A1) of total heavy metals accumulated in sediment. Factors with eigenvalues greater than 1 were taken into account. Two principal components (PCs) were extracted, explaining 78.166% of total variance in sediment dataset. Variable loading coefficients of the two principal components are listed in Table 4.21. The graphic representation of two components is also shown in Figure 4.40.

 Table 4.21. Matrix of the principal component analysis loading of metals and major elements of river sediment in location 2 Balok River.

Heavy Metal	Component			
	PC1	PC2		
Pb	0.924	0.310		
Mn	0.895	0.408		
Al	0.874	0.448		
Zn	0.832			
Fe	0.728	0.528		
Cr	0.395	0.501		
As	0.280	0.893		
Cd		0.846		
Cu	0.475	0.788		
Ni	-0.129	-0.440		
Eigenvalue	6.468	1.348		
% of Total Variance	64.680	13.486		
Cumulative% of variance	64.680	78.166		

^a Extraction Method: Principal Component Analysis; Rotation Method: Varimax with Kaisar Normalization.; Rotation converged in 3 iterations.

^b The boldfaced numbers are the dominant elements in different PCs

Component Plot in Rotated Space



Figure 4.40. Plot of loading PCA location 2 sediment in Balok River

The first PC, accounting for 64.680% of the total variance with an eigenvalues of 6.468% was correlated with Pb, Mn, Al, Zn, and Fe recorded absolute factor loading greater than 0.5 were 0.924, 0.895, 0.874, 0.832, and 0.728, respectively. This component can be termed to "natural factor" due to present of Mn, Fe and Al that lithogenic element. A lithogenic origin can be presumed in this component, since these heavy metals are in general present in the parent material soil. The pastures soils were sited in a river basin, and thus are considered an alluvial-coalluvial area (Uria *et al.*, 2009).

The second PC, accounting for 13.486%, of the total variance was next in significance with an Eigenvalue of 1.349%. The elements Fe, Cr, As, Cd and Cu, recorded absoluted factor loadings greater than 0.5 were 0.528, 0.501, 0.893, 0.846, and 0.788. This component can be termed to "anthropogenic factor" otherwise present of Fe is well known to be geogenic or lithogenic elements (Mico *et al.*, 2006), but present of Cr, As, Cd and Cu (Han *et al.*, 2006; Martin *et al.*, 2006) can affect the mobility of Fe in sediment river. Anthropogenic wastes such as wastewater from densely populated town

or wastes from paint, industries and shipbuilding manufacture are the important sources of Cd (Frickel and Elliott, 2008). High Cu values can come from Cu-based agrochemical related to specific agronomic practices, whereas vehicular and industrial fumes and wastewater used to irrigate some agricultural areas can also be the sources for the high Pb values found in some soil (Mico *et al.*, 2006).

4.11 Principal Component Analysis (PCA) on water in location 2

Principal component analysis has been carried out on the raw data (Appendix A3) of total heavy metals accumulated in sediment. Factors with Eigenvalues greater than 1 were taken into account. Two principal components (PCs) were extracted, explaining 76.462% of total variance in water data set. Variable loading coefficients of the two principal components are listed in Table 4.22. The graphic representation of two components is also shown in Figure 4.41.

Heavy Metal	Component			
	PC1	PC2		
Fe	-0.814			
Cd	0.753	0.202		
Al	0.911	0.189		
As	0.809	0.156		
Pb	0.759	0.411		
Ni	0.812	-0.217		
Cr	0.361	0.713		
Zn	0.411	0.602		
Mn		0.914		
Cu		0.805		
Eigenvalue	5.129	2.517		
% of Total Variance	51.294	25.172		
Cumulative% of variance	51 294	76 462		

Table 4.22 Matrix of the principal component analysis loading of metals and major elements of river water in location 2 Balok River. ^{a,b}

^a Extraction Method: Principal Component Analysis; Rotation Method: Varimax with Kaisar Normalization.; Rotation converged in 3 iterations.

^b The boldfaced numbers are the dominant elements in different PCs

The first PC, accounting for 51.294% of the total variance with an eigenvalues of 5.129% was correlated with Cd, Al, As, Pb, and Ni are recorded absolute factor loading greater than 0.5 were 0.753, 0.911, 0.809, 0.759, and 0.812, respectively while Fe had absolute Eigenvalue less than -0.5 was -0.814. This component can be termed to "anthropogenic activity" due to As, Pb and Zn related to human activity. Zn can have a lithogenic source as it forms a number of soluble salt (e.g., silicates, carbonates, phosponates, oxides, and sulphides) according to the prevailing pedogenic process (Adriano, 2001 and Mico *et al.*, 2006). However, Zn and its compounds are also used in different manufactured goods (e.g., paint, cosmetics, automobile tyres, batteries, and electrical apparatus) and in agricultural fertilizers (Mico *et al.*, 2006). Concern about the accumulation of Cd in the environment had resulted in some fertilizer manufacturers, encouraged by the European Union Commission, changing the sources of raw materials to reduce inputs (Nicholas *et al.*, 2003).



Figure 4.41. Plot of loading PCA location 2 water in Balok River

In this study, it seemed reasonable to conclude that Cd, Cr, Pb, As, and Zn constituted an anthropogenic component related to specific human activities, whereas the remaining elements (Fe, Al and Ni) appear to be associated of parent rocks. In the
case of Zn, this element displays a combined relationship with both groups and seems to have both natural and anthropogenic origin (Mico *et al.*, 2006).

The second PC, explanation 25.172%, of the total variance was next in significance with an Eigenvalue of 2.517%. The elements Cr, Zn, Mn and Cu, recorded absoluted factor loadings greater than 0.5. This component can be termed to "natural factor" due to Zn Mn, and Cu include to lithogenic elements. Mn is known well to be geogenic and Zn have both characteristic mainly natural and anthropogenic (Mico *et al.*, 2006). While, Cu may be related with slurry application indicated a combined origin lithogenic and anthropogenic, for this metal (Uria *et al.*, 2009).

4.12 Principal Component Analysis (PCA) on sediment in location 3

Two principal component analyses (PC1 and PC2) for sediment Balok River was determined Table 4.23. The grapic representation of two components is also shown in Figure 4.42. Two principal components (PCs) were extracted, explaining 75.901% of total variance in water dataset. The first component (PC1) explained 59.028% of the total variance with an Eigenvalue of 5.903 and dominated by Ni, As, Zn, Cr, Pb, Cu, and Mn, registered factor loadings greater than 0.5 mainly 0.945, 0.766, 0.764, 0.669, 0.666, 0.640, and 0.641, respectively. This component can be termed to "anthropogenic factor" due to combined Cr, Cu, Pb, Zn and As, otherwise Ni and Mn are well known lithogenic elements (Mico *et al.*, 2006) but Zn and Cu origin both natural and anthropogenic. This is can be reasoned that this component included to anthropogenic activity. Location 3 is Balok River upstream where there are many big chemical industries establish in this area such as Caltex, MTBE, BASF Petronas, BP Chemical, Kaneka, Estman Chemical, Cargil vegetable refinery, Polyplastic, etc.,

Heavy Metal		Component
	PC1	PC2
Ni	0.945	-0.287
As	0.766	0.275
Zn	0.764	0.367
Cr	0.669	0.408
Pb	0.666	0.430
Cu	0.640	0.412
Mn	0.611	0.545
Fe		0.938
Al	0.302	0.852
Cd	-0.419	-0.705
Eigenvalue	5.903	1.687
% of Total Variance	59.028	16.874
Cumulative% of variance	59.028	75.901

Table 4.23 Matrix of the principal component analysis loading of metals and major elements of river sediment in location 3 Balok River. ^{a.b}

Extraction Method: Principal Component Analysis; Rotation Method: Varimax with Kaisar Normalization.; Rotation converged in 3iterations. ^b The boldfaced numbers are the dominant elements in different PCs



Component Plot in Rotated Space

Figure 4.42. Plot of loading PCA location 3 sediment in Balok River

The second component (PC2) explained 16.874% of the total variance with eigenvalue of 1.687% and high values of Mn, Fe, Al and Cd recorded absolute factor loading greater than 0.5 were 0.545, 0.938, and 0.852 respectively while Cd had absolute Eigenvalues less than -0.5 was -.0705. This component can be termed to "natural factor' due to Fe, Mn, and Al are well known lihogenic elements (Mico *et al.*, 2006) and present of Cd indicated influence natural factor otherwise Cd is related human activity. The accumulation of heavy metals in sediments can be a secondary source of water pollution once environmental condition change (Chen *et al.*, 1996; Cheung *et al.*, 2003 and Hang *et al.*, 2009).

4.13 Principal Component Analysis (PCA) on water in location 3

Three principal components were obtained with Eigenvalues >1, explaining 76.022% of total variance in water dataset. Variable loading coefficients of the three principal components are listed in Table 4.24. The graphic representation of three components is also shown in Figure 4.43. The first PC, accounting for 40.742% of the total variance with an eigenvalues of 4.074% was correlated with Zn, As, Cu and Cd recorded absolute factor loading greater than 0.5 were 0.847, 0.707, 0.660, and 0.704, respectively. This component can be termed "anthropogenic activity" due to present of Zn, As, Cu, and Cd related to human activity.

Heavy Metal	Component		
	PC1	PC2	PC3
Zn	0.847	0.109	-0.164
As	0.707	0.386	0.231
Cu	0.660	0.224	0.372
Cd	0.704	-0.129	-0.620
Mn	0.402	0.903	0.233
Cr		0.766	
Pb	0.317	0.848	
Al	0.244	0.719	-0.337
Ni	-0.155		0.814
Fe	0.414		0.782
Eigenvalue	4.074	2.001	1.510
% of Total Variance	40.742	20.093	15.187
Cumulative% of variance	40.742	60.835	76.022

Table 4.24. Matrix of the principal component analysis loading of metals and major elements of river water in location 3 Balok River.^{ab}

^a Extraction Method: Principal Component Analysis; Rotation Method: Varimax with Kaisar Normalization.; Rotation converged in 5 iterations.

^b The boldfaced numbers are the dominant elements in different PCs

Component Plot in Rotated Space



Figure 4.43. Plot of loading PCA location 3 water in Balok River

The second PC explained 20.093% of the total variance with an eigenvalues 2.009% and dominated by Mn, Cr, Pb and Al. The third PC, accounting for 15.187% of the total variance with an eigenvalues 1.519%, was weighted only Ni and Fe, was positive correlated factor loading greater than 0.5 were 0.814 and 0.782, respectively, and Cd had absolute Eigenvalues less than -0.5 was -0.642. PC2 and PC3 explained that lithogenic factor dominated the distribution of most part of the considered elements in this area.

4.14 Quantification of stream sediments pollution Balok River

The Enrichment Factors (EF) for the streams sediment all of sampling point in Balok River were presented in Table 4.25 and illustrated in Figure 4.44.

Element	Logation 1	Logation 2	Location 2
Element	Location 1	Location 2	Location 5
Al	0.822±0.171	1.154 ± 0.182	0.953 ± 0.169
Cr	0.788±0.427	1.414±0.475	1.412±0.438
Mn	0.269 ± 0.084	0.230±0.074	0.176±0.022
Fe	1.000 ± 0.000	1.000 ± 0.000	1.000 ± 0.000
Ni	0.355±0.219	0.531±0.439	0.360±0.149
Cu	0.482±0.126	1.069±0.360	1.141±0.222
Zn	0.886 ± 0.778	1.528±0.418	1.030±0.059
As	9.686±1.725	8.147±2.943	7.641±1.346
Cd	9.465±2.925	52.532±12.163	19.606±6.699
Pb	6.688±5.364	3.276±0.929	5.501±1.464

Table 4.25. Enrichment Factors for stream sediments of study area.

The results showed that all the stream sediments are significantly enriched with Cd with EF range of 9.465-52.532. All the stream sediments with respect to Al, Cr, Mn, Ni, Cu and Zn had enrichment factors of less than 2 and can therefore be classified as deficiency to minimal enrichment, that considered being in the range of natural variability (Hernandez *et al.*, 2003). The Enrichment Factor values also indicate that As enrichment factor values ranging between 5 until 20, can therefore be classified as significant enrichment, Cd enrichment factor values ranging between (2 until 5) and (5 until 20), can therefore be classified as significant enrichment. Based on (Hernandez *et al.*, 2005; Salati and Moore 2010) revealed that EF values were > 2 indicating anthropogenic impact on metal concentration in the river. Pb enrichment factor values ranging between 2 until 5 can therefore be classified as moderate enrichment corresponding mainly to the anthropogenic (Hernandez *et al.*, 2005).

Arsenic has the second highest EF with value of 7.641– 9.686 (average 8). The percentage of studied locations with EF>2 in sediments was represented in Figure 4.46, which showed that the sediments of location 1, 2, and 3 of Balok River can be regarded as unpolluted with Al, Cr, Mn, Fe, Ni, Zn, and Cu. On the other hand, a serious contamination of these sediments may be discussed for As, Cd and Pb because the concentrations of these metals were higher than twice their background in 16%, 25% and 27% of the investigated samples. This suggests that metals are from anthropogenic inputs, including industries manufacturing textile, cement, petrochemical industry and domestic waste water. The difference in EF values for different metals in sediments may be due to the difference in the magnitude of input for each metal in sediment and/or the difference in the removal rate of each metal from the sediments (Ghrefat *et al.*, 2010).

Enrichment of As, Pb and Cd indicated especially at locations within the urban area. Higher enrichment of As was particularly notable for location 1 and 2 receiving effluents from Residential Balok Perdana, chemical industry and downstream Nyior River that contain heavy metal waste. Location 1 and 2, appear to be significantly enriched with As. The highest EF value of 9.686 for As was recorded in location 1. Cadmium appeared to be enrichment in location 3 than location 1 due to near the effluent factory. The EF values of Cd for location 1, 2, and 3 were 9.465, 52.532, and 19.606, respectively. Plumbum was significantly enriched in location 1 with EF value 5.31. Value of Enrichment Factor presented in Figure 4.44.



Figure 4.44. Enrichment Factor (EF) in sediment in sampling sites of Balok River

The Contamination Factor (CF) and Pollution Load Index (PLI) all of location in Balok River are shown in Table 4.26, illustrated Contamination Factor and Pollution Load Index in Figure 4.45 and 4.46, respectively.

Element	Location 1	Location 2	Location 3
Al	0.098±0.042	1.573±0.043	1.303±0.066
Cr	0.089±0.018	1.933±0.054	1.619±0.047
Mn	0.025 ± 0.013	0.387±0.002	0.247±0.009
Fe	1.291±0.004	1.696±0.043	1.276±0.071
Ni	0.317±0.007	0.616±0.039	0.457 ± 0.007
Cu	0.562±0.011	0.168±0.021	1.386±0.067
Zn	0.704±0.012	2.143±0.046	2.807±0.041
As	1.049±0.629	2.669 ± 0.204	1.016 ± 0.448
Cd	1.943±1.943	4.398±1.004	1.903±0.520
Pb	0.432±0.165	0.678±0.242	0.766±0.356
Pollution Load Index (PLI)	0.355	1.134	1.057

 Table 4.26. Contamination Factor and Pollution Load Index of stream sediment

The CFs result shows that all the streams have high levels of Cd in their sediments in the order: Location 2 (4.398±1.004)> Location 1 (1.943±1.943)> Location 3 (1.903 \pm 0.520)>. Location 2 sediment recorded the highest CF value of 1.696 \pm 0.043 for Fe whereas Location 1 garnered a CF value 1.291±0.004 then location 3 garnered a CF value 1.276±0.071. The highest CF value (2.669±0.204) for As was found at location 2 sediment samples. The CF values of As recorded for location 1 and location 3 sediments were 1.049±0.629 and 1.016±0.448, respectively. Location 3 had the highest CF value for Zn (2.807±0.041) and location 2 followed with 2.143±0.046. Location 1 for Zn less than 1.0 was 0.704 ± 0.012 . Location 3 recorded the highest (1.386 \pm 0.067) CF value for Cu. The rest of the stream sediments recorded CF values less than 1.0 for Cu mainly location 1 and location 2 were 0.562±0.011 and 0.168±0.021, respectively. The highest CF for Pb (0.432±0.165) was detected in location 1. The CF values for Pb for location 2 and location 3 sediments were computed to be 0.678±0.242 and 0.766±0.356, respectively. Apart from location 1 which retained Ni CF value slightly all the rest of the examined streams had values less than 1, where location 1, location 2 and location 3 were 0.317±0.007, 0.616±0.039 and 0.457±0.007, respectively. Location 2 recorded of Mn CF value of 0.387 ± 0.002 , followed by location 3 (0.247 ± 0.009) and location 1 (0.025±0.013), respectively. Location 1, location 2 and location 3 had Mn CF values less than 1.0 for their sediments. The CF values of Cr recorded for location 2 and location 3 sediments were 1.933±0.054 and 1.619±0.047, respectively. Location 1 recorded CF values less than 1.0 for Cr by 0.089±0.018. Location 1 had Al CF values less than 1.0 for their sediments was 0.098±0.042 whereas location 2 and location 3 had more than 1.0 for their sediments were 1.573±0.043 and 1.303±0.066, respectively. Figure 4.45 shown value of contamination factor sediment of Balok River.

The sampling points show variations in the PLI values. However, all of the sampling points have the PLI values <1.0 for location 1 while location 2 and 3 have the PLI values 1 (table 4.20). This value is indication of "unpollutant" within grade 1 for location 1, while for location 2 and 3 are indication "baseline levels of pollutant present" within grade 2. The overall Pollution Load Indices for the stream sediments were found to be in the order: Location 2 (PLI = 1.134) > location 3 (PLI = 1.057) >



location 1 (PLI=0.355). A comparative diagram of the PLI values in stream sediment samples is presented by Fig.4.46.

Figure 4.45. Contamination Factor sediment of Balok River



Figure 4.46. Comparison of Sediment Pollution Load Indices of examined streams

The Contamination Factor and Pollution Load Index (PLI) of the study area in Balok River as shown in Table 4.27, depicted in Figure 4.47 and Figure 4.48, respectively.

Element	Location 1	Location 2	Location 3	
Al	8.387±5.126	18.344±7.218	8.690±2.248	
Cr	4.037±2.614	1.639 ± 0.427	0.280±0.057	
Mn	0.331±0.124	0.873±0.295	0.428 ± 0.025	
Fe	102.766±48.377	85.237±28.436	63.608±20.104	
Ni	0.248±0.103	0.721±0.455	0.458±0.113	
Cu	2.308±0.484	0.912±0.152	0.518±0.029	
Zn	0.716±0.296	2.065±0.094	2.178±0.218	
As	15.377±6.055	21.112±10.125	23.025±8.291	
Cd	21.669±15.873	27.009±15.602	12.727±4.007	
Pb	7.194±4.386	9.967±2.371	10.089±3.824	
Pollution Index				
Load (PLI)	3.221	3.198	2.495	

Table 4.27. Contamination Factor and Pollution Load Index of stream water

The CFs result shows that all the location have high levels of Fe in their water in the order: location 1 (102.766±48.377)> location 2 (85.237 ± 28.436)> location 3 (63.608 ± 20.104). Location 2 water recorded the highest CF value (27.009 ± 15.602) for Cd whereas location 1 garnered a Cd CF value of (21.669 ± 15.873) and last location 3 registered Cd CF values 12.727±4.007. The highest CF value (23.025 ± 8.291) for As was found at location 3 water samples. The CF values of As recorded for in location 1 and 2 water samples were (15.377 ± 6.055) and (21.112 ± 10.125), respectively. Location 2 had the highest CF value for A1 (18.344 ± 7.218), and location 3 followed with (8.690 ± 2.248), and location 1 recorded CFs for Al (8.387 ± 5.126). Location 1 recorded CF value of (4.037 ± 2.614), followed by location 2 (1.639 ± 0.427), and location 3 (0.280 ± 0.057). Location 1, 2 and 3, recorded CF values less than 1.0 for Mn, Ni, and Zn. Location 2 and 3 recorded CF values less than 1.0 for Cu whereas location 1 recorded CF values less than 1.0 for Mn, Ni, and Zn. Location 2 and 3 recorded CF values less than 1.0 for Cu whereas location 1 recorded CF values less than 1.0 for Mn, Ni, and 2.308\pm0.484. All of CF of water Balok River presented in Figure 4.47.

The sampling points show variations in the PLI values. However, all of the sampling points have the PLI values >1.0 (table 4.25). This values are indication of "Baseline level of pollutant" within grade 2. The overall Pollution Load Indices for the stream water sample were found to be in the order: Location 1 (PLI = 3.221) > location 2 (PLI = 3.198) > location 3 (PLI=2.495). A comparative diagram of the PLI values in stream water samples is presented by Fig.4.48.



Figure 4.47. Contamination factor in water sampling sites of Balok River



Figure 4.48. Comparison of water Pollution Load Indices of examined streams

4.15 Water Quality Parameters Analysis for Tunggak River

The overall water quality results and the average water quality results at the three sampling points for the Tungak River during November 2010 until November 2012 presented in Table 4.28. The results were then compared to the DOE Interim National Water Quality Standards for Malaysia (INWQS). The INWQS can be refered to Appendix 17.

Station	рH	COD	BOD	DO	SS	AN
	r			_		
1	663+076	22.93+2.78	542+115	5 76+0 79	38 18+4 80	0.29 ± 0.04
-	0.05_0.70	22.75_2.76	5.12_1.15	5.10_0.19	50.1021.00	0.27_0.01
2	626+077	28 82+5 44	8 87+1 81	331+0.47	50.94+5.55	0.44 ± 0.03
2	0.20±0.77	20.02-5.77	0.07±1.01	5.51±0.77	50.74±5.55	0.77±0.05
3	6 12+0 66	29.00+5.7	10 43+2 15	264+049	71 76+6 21	0.82 ± 0.07
5	0.12 ± 0.00	27.00-5.7	10.45±2.15	2.07±0.77	/1./0±0.21	0.02-0.07

 Table 4.28 Result of six water quality parameters

4.15.1 Chemical Oxygent Demand

In this study the concentrations of COD observed for station 1, 2 and 3 of Tunggak River were 22.93 ppm, 28.82 mg/L and 29.00 ppm, respectively, shown in Figure 4.49. Based on the maximum recommended INWQS, threshold level COD for Malaysia Rivers is 100 ppm (Appendix A-17). The average values of COD for location 2 and 3 of the river systems were within the INWQS threshold level for class III except location 1 was class II. Therefore, the Tunggak River is safe for domestic water supply and irrigation only after future extra treatment.



Figure 4.49. The average chemical oxigent demand values for 3 sampling point along of the Tunggak River

4.15.2 Biological Oxygen Demand

Based on figure 4.50, it is found that the highest average reading of BOD was at location 2 and 3 with the reading 8.87 ppm and 10.43 ppm, respectively and it was

INWQS threshold level for class III. Based on the results, it could be presumed that, at location 1 and 3 the BOD indicating the highest reading may due to that may probably increase the BOD reading at selected point. On the contrary, the lowest reading of BOD at location 1 with the reading of 5.42 ppm was within INWQS threshold level for class II. Thus, the water at the catchments area is doubt to be harmful and contaminated.



Figure 4.50. The average biological oxygent demand values for 3 sampling point along of the Tunggak River

4.15.3 Dissolved Oxygent

The average concentrations of DO for location 1, 2, and 3 at Tunggak River were 5.43 ppm, 3.62 ppm and 2.54 ppm, respectively, as shown in Figure 4.51. From the figure, the differences of DO concentration recorded during the study at different sampling site along Tunggak River can be seen. Location 1 and 2 of Balok Rivers showed DO values within the class II of INWQS thereshold level to support of aquatic



life. While at location 1 theDO value was within the INWQS thereshold level for class I.

Figure 4.51. The average dissolved oxygen values for 3 sampling point along of the Tunggak River

4.15.4 Ammoniacal Nitrogent

Figure 4.52 shows that the highest average reading of Ammoniac Nitrogen was 0.82 ppm and within class III of INWQS occurred at location 3 of Tunggak River. Meanwhile the lowest concentration average of AN was 0.19 ppm within the class II of INWQS occurred at location 1 of Tunggak River most likely due to its location which is located at the downstream of the catchments area and therefore less organic contaminants present. Meanwhile at location 2, the AN was 0.44 ppm and was within class II of INWQS.



Figure 4.52. The average Amoniac Nitrogen values for 3 sampling point along of the Tunggak River.

4.15.5 Suspended Solid

Based on the maximum recommended INWQS threshold level SS for Malaysia Rivers is >300 ppm (Appendix A-17). The average values of SS for location 1 (38.18 ppm) and 2 (50.94 ppm) of the river systems were within the INWQS threshold level for classes 1 except location 3 (71.76 ppm) presented on Figure 4.53. Therefore, the water of Tunggak River systems is safe for domestic water supply, irrigation after extra treatment.



Figure 4.53. The average Suspended Solid values for 3 sampling point along of the Tunggak River.

4.15.6 pH

Based on the result it clearly shows that the lowest average pH values was indicated on the location 3 with the average pH value of 6.1. Meanwhile, the highest average pH value was indicated at the location 1 with the average pH value of 6.63. Based on the results of pH in every sampling station at each sampling time, it shows that the changing pattern of pH value were moderately unvarying.

From the graph, it clearly shows that the average value results for pH at every sampling point were initially high at location1 because less contamination affecting to the water, and slightly drop at location 2 and location 3. The average pH at location 2 is 6.26, nearly neutral but less than 7 and indicates the water in acidic condition, because location 2 are located at downstream of catchments. For the location 1 near mouth of river and less human activity. Meanwhile, at location 3, the average value results for pH are decrease to 5.29 that indicates much acidic condition because \leq than 5. This might

be due to its location located exactly after the industrial area, whereby the direct discharged of wastewater to the catchments has affected the decreasing value of the water pH.



Figure 4.54. The average pH values for 3 sampling point along of the Tunggak River.

4.15.7 Water Quality Index (WQI)

The value of the water quality index (WQI) is determined by first obtaining the sub index value for each parameter. The WQI is good indicator of any deterioration or improvment of a water body. Based on Table 4.29 and Figure 4.55. it shows that the sub index for WQI in station 1, 2, 3 of Tunggak River were 81, 69, and 66, respectively. Among the three staions, the WQI for station 1 is the highest. This is mainly due to its surrounding contain the lowest industrial activity while the remaining stations were surrounded with residential and industrial areas and other land use. From the value derived from the sub index, station 1 of Tunggak River is classified as Class II which is clean area. This is because surrounding of river systems has a lot of trees that can help to reduce river pollution. Meanwhile from the value derived from the sub index, location 2 and 3 is classified as Class II which is slight polluted.

Table. 4.29. Status of River Pollution on Water Quality Index (WQI) and Sub Index for Tunggak River

Station	SIpH	SIDO	SIBOD	SICOD	SISS	SIAN	WQI	Status
1	98	94	77	71	77	70	81	Clean
2	94	85	64	64	72	65	69	Slight Polluted
3	60	66	22	65	64	53	66	Slight Polluted



Figure 4.55 Water Quality Index of sampling site of Tunggak River performace

4.16 Heavy Metal Concentration in Water and Sediment in Tunggak River

The sample was taken between November 2010 until November 2012 water and sediment samples have taken November 2010 until July 2011 with successful. The mean concentrations of 10 heavy metals (Al, Cr, Mn, Fe, Ni, Cu, Zn, As, Cd, and Pb) in

location 1, location 2, and location 3 along Tunggak River water and sediment samples are illustrated in Appendix A9-A12.

For the water samples, the highest average Al concentration of 0.99 ppm was recorded at location 3, followed by location 2 at 0.63 ppm and the lowest at location 1 with concentration of 0.52 ppm. The maximum recommended of INWQS threshold level of aluminum for Malaysia Rivers is 0.5 ppm (Appendix A-17). In this study, the average values of aluminum for location 1 of the river systems were within the INWSQ for class IV, while location 3 and 2 were above INWQS (Figure 4.56).

For sediment, the highest deposit of Al was found to be at location 2 with the concentrations of Al 12209.30 ppm ppm. The average Al concentration in location 3 sediment was 9913.55 ppm. The reference location 1 sediment recorded Al concentration of 6579.83 ppm. A high level of detected shows that the sediments is polluted and could be due to the high discharged of effluent contained with aluminum from the massive industrial activities along the river bank such as electroplating, printing factor and also might be contributed by the occurrences of natural process.



Figure 4.56. Average aluminum values for 3 sampling points of the Tunggak River systems

In this study, the presence of Cr in water samples for location 1, 2 and 3 were detected at concentrations 0.32 ppm, 1.42 ppm and 0.11 ppm were reported for location 1, 2 and 3, respectively. Based on the maximum recommended INWQS threshold level chromium for Malaysia Rivers is 0.1 ppm (Appendix A-17). The average values of chromium for location 2 and 3 of the river systems were not within the INWQS threshold level for all classes except location 1 (Figure 4.57). From this figure, it can be conducted that the water of Tunggak River is safe for domestic water supply and irrigation only after extra treatment is undertaken.

Meanwhile, the amount of Cr in location 1, 2 and 3 along Tunggak river sediments were 6.570 ppm, 10.02 ppm and 11.70 ppm, respectively. Generally, the present of Cr in sediment came from the chemical and metallurgical industry for the production of stainless steel and other alloys steels, and in the refractory. Hence, the water of Tunggak River systems is believed to be unsuitable for the supply of water for domestic, industrial and agricultural purposes as the concentrations of Cr detected is already above allowed limitations by INWQS. Furthermore, the Tunggak River could be classified as polluted and may risk the aquatic life of the river ecosystems.



Figure 4.57. Average chromium values for 3 sampling points of the Tunggak River systems

In this study, the presence of Mn in water samples for location 1, 2 and 3 were detected at concentrations 0.43 ppm, 0.39 ppm and 0.63 ppm were reported for location 1, 2 and 3, respectively. Based on the maximum recommended INWQS threshold level Manganese for Malaysia Rivers is 0.2 ppm (Appendix A-17). The average values of chromium for location 1, 2 and 3 of the river systems were not within the INWQS threshold level for classes IV (Figure 4.58). From this figure, it can be conducted that the water of Tunggak River is safe for domestic water supply and irrigation only after extra treatment is undertaken.

Meanwhile, the amount of Mn in location 1, 2 and 3 along Tunggak river sediments were 41.91 ppm, 44.22 ppm and 62.48 ppm, respectively. Generally, the present of Mn in sediment came from the chemical and metallurgical industry for the production of stainless steel and other alloys steels, and in the refractory.



Figure 4.58. Average manganese values for 3 sampling points of the Tunggak River systems

Location 3 registered the highest Fe levels in both water and sediment samples. The average Fe concentration 7032.55 ppm in sediment samples of location 3 was the highest and location 2 was next with 6387.35 ppm whereas location 1 recorded the lowest of 5103.51 ppm. Average Fe level in water samples of location 3 was highest 3.43 ppm, followed by location 1 was 9.32 ppm and location 2 recording the lowest level of 5.54 ppm. The maximum recommended INWQS threshold level of Fe for Malaysian rivers is class IV mainly 5 ppm (Appendix A-17). The average values of Fe for all the sampling points of the Tunggak River within the INWQS threshold level only for location 1, whilst for location 2 and 3 exit above INWQS level (Figure 4.59). In terms of ferrum, the river waters of Tunggak River systems were unsuitable for the support of aquatic life and supply water domestic, industrial, and agricultural uses for the above mentioned and sampling points except after extra treatment. High level of ferrum in water Tunggak River may be from natural and anthropogenic sources but increasing of industry that uses heavy metal in the high amount can be an influence increasing of Fe in water river systems.



Figure 4.59. Average ferrum values for 3 sampling points of the Tunggak River systems

For the water samples, the highest average Ni concentration of 0.07 ppm was recorded at location 1, followed by location 2 at 0.06 ppm and the lowest at location 3 with concentration of 0.05 ppm. The maximum recommended of INWQS threshold level of Nickel for Malaysia Rivers is 0.9 ppm (Appendix A-17). In this study, the average values of Nickel for all sampling points of the river systems were within the INWSQ for class II (Figure 4.60). In terms of Ni, the river waters of Tunggak River systems were suitable for the supply of water for domestic, industrial and agricultural uses after treatment for the above mentioned sampling points

For sediment, the highest deposit of Ni was found to be at location 2 with the concentrations of Ni 6.04 ppm. The average Ni concentration in location 3 sediment was 6.94 ppm. The reference location 1 sediment recorded Ni concentration of 2.85 ppm.





In this study, the presence of Cu in water samples for location 1, 2 and 3 were detected at concentrations 0.07 ppm, 0.08 ppm and 0.27 ppm were reported for location

1, 2 and 3, respectively. Based on the maximum recommended INWQS threshold level Copper for Malaysia Rivers is 0.2 ppm (Appendix A-17). The average values of chromium for location 1, 2 and 3 of the river systems were within the INWQS threshold level for classes IV (Figure 4.13). From this figure, it can be conducted that the water of Tunggak River is safe for domestic water supply and irrigation only after extra treatment is undertaken.

Meanwhile, the amount of Cu in location 1, 2 and 3 along Tunggak river sediments were 2.63 ppm, 3.54 ppm and 6.88 ppm, respectively. All these sampling points are located at the Tunggak River which is a crowded industrial zone and there are many chemical industries there. This show the major sources of Cu in the water body Tunggak River were probably contributed by the industries located at the upstream of the river. Water body Tunggak River that contains heavy metal flow to downstream and contaminates any location that flowed until to the mouth of the river



Figure 4.61. Average copper values for 3 sampling points of the Tunggak River systems

In this study, the presence of Zn in water samples for location 1, 2 and 3 were detected at concentrations 1.26 ppm, 0.98 ppm and 0.33 ppm were reported for location 1, 2 and 3, respectively. Based on the maximum recommended INWQS threshold level Zinc for Malaysia Rivers is 5 ppm (Appendix A-17). The average values of Zinc for location 1, 2 and 3 of the river systems were within the INWQS threshold level for classes II (Figure 4.62). From this figure, it can be conducted that the water of Tunggak River is safe for domestic water supply, industrial and agricultural uses after treatment. Meanwhile, the amount of Zn in location 1, 2 and 3 along Balok river sediments were 26.39 ppm, 33.89 ppm and 72.42 ppm, respectively.



Figure 4.62. Average zinc values for 3 sampling points of the Tunggak River systems

In this study, the presence of As in water samples for location 1, 2 and 3 were detected at concentrations 0.15 ppm, 0.21 ppm and 0.28 ppm were reported for location 1, 2 and 3, respectively. Based on the maximum recommended INWQS threshold level As for Malaysia Rivers is 0.4 ppm (Appendix A-17). The average values of As for location 1, 2 and 3 of the river systems were within the INWQS threshold level for

classes IV (Figure 4.63). From this figure, it can be conducted that the water of Balok River is safe for domestic water supply, industrial and agricultural uses after treatment. Meanwhile, the amount of As in location 1, 2 and 3 along Balok river sediments were .50 ppm, 1.83ppm and 1.60 ppm, respectively.



Figure 4.63. Average arsenic values for 3 sampling points of the Tunggak River systems

In this study, the presence of Cd in water samples for location 1, 2 and 3 were detected at concentrations 0.06 ppm, 0.01 ppm and 0.07 ppm were reported for location 1, 2 and 3, respectively. Based on the maximum recommended INWQS threshold level Cadmium for Malaysia Rivers is 0.01 ppm (Appendix A-17). The average values of Cadmium for location 1 and 3 of the river systems were not within the INWQS threshold level for all classes except location 2 (Figure 4.13). The levels of Cd in the water of Tunggak River systems were not considered for human exposure otherwise after treatment due to Cd high toxicity for human. Meanwhile, the amount of Cd in location 1, 2 and 3 along Tunggak river sediments were 0.13 ppm, 0.13 ppm and 0.15 ppm, respectively.



Figure 4.64. Average cadmium values for 3 sampling points of the Tunggak River systems

In this study, the presence of Pb in water samples for location 1, 2 and 3 were detected at concentrations 0.54 ppm, 0.34 ppm and 0.66 ppm were reported for location 1, 2 and 3, respectively. Based on the maximum recommended INWQS threshold level Plumbum for Malaysia Rivers is 5 ppm (Appendix A-17). The average values of Plumbum for location 1, 2 and 3 of the river systems were within the INWQS threshold level for all classes (Figure 4.65). Meanwhile, the amount of Pb in location 1, 2 and 3 along Tunggak river sediments were 6.38 ppm, 4.58 ppm and 7.59 ppm, respectively.



Figure 4.65. Average plumbum values for 3 sampling points of the Tunggak River systems

The elemental concentrations determined in sediment for each sampling were presented in Appendix A9 –A12. The trend of heavy metal concentrations in sediments from the Tunggak river system for each of the sampling sites within three times sampling were determined and presented in Table 4.30. Besides that, the average concentrations of heavy metals in sediments for all the sampling points and the average concentration of heavy metals for the three samplings are listed in Table 4.31.

All in All, the dominance of various heavy metals in the surface sediment of the Tunggak river followed the sequence: Al>Fe>Mn>Zn>Cr>Pb>Ni>Cu>As>Cd. This indicates that aluminum is the highest concentration of heavy metals and Cadmium is the lowest concentration of heavy metal found in sediments determined in all 3 times samplings and all sampling points.

All heavy metals concentrations in this study in the sediment at each sampling point were presented in Appendix A1 –A4. The trend of heavy metal concentrations in sediments from the Tunggak River for each of the sampling sites within seven times sampling is presented in Table 4.30. Meanwhile Table 4.31 listed the average concentrations of heavy metals in sediments for all the sampling. It can be summarized that the dominance of various heavy metals in the surface sediment of the Tunggak river as the following: Al>Fe>Mn>Zn>Pb>Cr>Ni>Cu>As>Cd. This indicates that aluminum is dominant and Cadmium is the less dominant found in sediments at all sampling points.

Table 4.30. Trend of heavy metals in sediment for the three samplings sites in TunggakRiver during November 2010, March 2011 and July 2011

Sampling si	te Trend of	f heavy metal		
Location 1	Al>Fe>N	/In>Zn>Cr>Pb>Ni>	>Cu>As>Cd	
Location 2	Al>Fe>N	/In>Zn>Cr>Ni>Pb>	>Cu>As>Cd	
Location 3	Al>Fe>Z	Zn>Mn>Cr>Pb>Ni>	>Zn>As>Cd	

Table 4.31. Average of heavy metals concentration in sediment (ppm) for the three samplings in Tunggak River sites during November 2010, March 2011 and July 2011

Elements	Al	Fe	Mn	Zn	Cr	Pb	Ni	Cu	As	Cd
Average (ppm) 9567.60	6174.50	49.54	44.24	9.43	6.19	5.25	4.38	1.97	0.14
Trend	Al>	Fe>	Mn>	Zn >	Cr >	Pb>	Ni>	Cu>	As>	Cd

All heavy metals concentrations in this study in the sediment at each sampling point were presented in Appendix A1 –A4. The trend of heavy metal concentrations in sediments from the Tunggak River for each of the sampling sites within seven times sampling is presented in Table 4.30. Meanwhile Table 4.31 listed the average concentrations of heavy metals in sediments for all the sampling. It can be summarized that the dominance of various heavy metals in the surface sediment of the Tunggak river as the following: Al>Fe>Mn>Zn>Cr>Pb>Ni>Cu>As>Cd. This indicates that

Aluminum is dominant and Cadmium is the less dominant found in sediments at all sampling points.

The elemental concentrations determined in water for each sampling were presented in Appendix A9-A12. Based on that, the trend of concentration of heavy metals in water for each of the samplings was presented in Table 4.32. Besides that, the average concentrations of heavy metals in water for all the sampling points are listed in Table 4.33. Generally, the concentrations of the elements in the river sediments were higher than that of the water samples. All in All, the dominance of various heavy metals the surface water the Tunggak river followed in of the sequence: Fe>Zn>Al>Cr>Pb>Mn>As>Ni>Cu>Cd. Based on the trend of heavy metals according to average value of all sampling points in Table 4.33, Ferrum is the highest concentration of metal among all the sampling points in the Tunggak river water. Thus, ferrum is the highest concentration found in the Tunggak river water, and Cadmium is the lowest concentration in the Tunggak river water.

Table 4.32. Trend of heavy metals in water for the three samplings sites during inTunggak River November 2010 until November 2012

Sampling site	Trend of heavy metal
Location 1	Fe>Al>Mn>As>Zn>Cr>Cu>Cd>Pb>Ni
Location 2	Fe>Cu>Zn>Al>Mn>Pb>As>Cu>Ni>Cd
Location 3	Fe>Ni>Al>Zn>Mn>Pb>Cu>As>Cr>Cd

Table 4.33. Average of heavy metals concentration in water (ppm) for the three samplings sites in Tunggak River during November 2010 until November 2012

Elements	Fe	Zn	Al	Cr	Pb	Mn	As	Ni	Cu	Cd
Average (ppm)	6.10	0.86	0.74	0.62	0.51	0.48	0.21	0.14	0.06	0.04
Trend	Fe>	Zn>	Al>	Cr>	Pb>	Mn>	As>	Ni>	Cu>	Cd

In general, the concentrations of the elements in the sediment samples are higher than that of the water, and this might be since the fact that metals can be either transported by the water or suspended sediment stored within the riverbed bottom sediment (Adomako *et al.*, 2008; Garbarino, 1995).

In the bottom sediments, the distribution of heavy metals is affected by mineralogical and chemical composition of suspended material, anthropogenic influences, and in situ process such as deposition, sorption, and enrichment in organism (Forster and Muller, 1975; Jain *et al.*, 2005). Chemical leaching of bedrocks, water drainage basins, and runoff from banks are the primary sources for the lithogenic contribution of heavy metals. Discharge of urban and industrial waste water, agricultural activities, combustion of fossil fuels, mining and smelting operations, processing and manufacturing, industries, waste disposal including dumping, etc., are primary anthropogenic sources of pollution (Klavins *et al.*, 2000; Yu *et al.*, 2001; Shakeri and Moore, 2010).

4.17. Heavy metal concentrations in water and sediment of three sampling stations of Tunggak River.

Heavy metal concentrations in water and sediments of Tunggak River were determined at three sampling stations namely location 1 (joint Balok River), location 2 (sewage of residential and industry activities) and location 3 (sewage of Industry Gebeng Area and road), for the study period (November 2010 until November 2012). ANOVA was used to compare the differences among them as depicted in Appendix A1-A4. The recorded values of the heavy metal concentrations in water and sediment samples are shown in Table A-13 to A-16 of Appendix A.

1. Aluminum

The distribution of Al concentrations in water and sediment at three sampling points are showed in Figure 4.66 and 4.67. The average of Al concentrations in water varied from 0.596±0.120 ppm in location 1, 0.630±0.218 ppm in location 2, and

 1.021 ± 0.588 ppm in location 3. Average of Al concentrations in sediment varied from 6572.063 ± 996.048 ppm in location 1, while 12209.229 ± 2079.140 mg/kg in location 2 and 9913.554 ± 1192.526 ppm in location 3. When comparing of Al concentrations in three sampling point it was found that differences were not statistically significant (P>0.05) for water and were statistically significant (P<0.05) for sediment.

The average Al concentrations in water varied in November 2010 to 0.004 ± 0.002 ppm, in March 2011 to 1.160 ± 0.624 ppm and in July 2011 to 0.625 ± 0.199 ppm, in July 2012 to 0.410 ± 0.043 ppm, in September 2012 to 0.998 ± 0.412 ppm, in October 2012 to 0.918 ± 0.298 ppm, and in November 2012 to 1.089 ± 0.077 ppm. Average of Al concentrations in sediment varied in November 2010 to 9206.471±3600.017 ppm, in March 2011 to 9101.032±1147.263 ppm and July 2011 to 10607.423±3538.285 ppm. After comparing of Al concentrations during 7 times in a year, it was found that the differences were statistically (P<0.05) for water and were not statistically significant (P>0.05) for sediment.







Figure 4.67 Al concentrations in water of three sampling stations of Tunggak River during November 2010 until November 2012

2. Chromium

The distribution of Cr concentrations in water and sediment at three sampling points are shown in Figure 4.68 and 4.69. The average of Cr concentrations in water varied from 0.318 ± 0.042 ppm in location 1, 1.424 ± 0.390 ppm in location 2, and 0.109 ± 0.019 ppm in location 3 and average of Cr concentrations in sediment varied from 6.570 ± 1.070 ppm in location 1, while 10.018 ± 0.574 ppm in location 2 and 11.700 ± 0.660 ppm in location 3. When comparing of Cr concentrations in three sampling point it was found that differences were not statistically significant (P>0.05) for water and were statistically significant (P<0.05) for sediment.

The average Cr concentrations in water varied in November 2010 to 0.003 ± 0.001 ppm, in March 2011 to 1.745 ± 0.631 ppm, in July 2011 to 0.797 ± 0.352 ppm, in July 2012 to 0.214 ± 0.026 ppm, in September 2012 to 0.194 ± 0.087 ppm, in

October 2012 to 2.083 ± 0.279 ppm and in November 2012 0.637 ± 0.189 ppm. Average of Cr concentrations in sediment varied in November 2010 to 9.047 ± 2.897 ppm, in March 2011 to 9.385 ± 2.819 ppm and July 2011 to 9.856 ± 2.364 ppm. After comparing of Cr concentrations during 7 times in a year, it was found that the differences were not significant (P>0.05) for sediment and water.



Figure 4.68 Cr concentrations in sediment of three sampling stations of Tunggak River during November 2010 until July 2011



Figure 4.69 Cr concentrations in water of three sampling stations of Tunggak River during November 2010 until November 2012

3. Manganese

The distribution of Mn concentrations in water and sediment at three sampling points are shown in Figure 4.70 and 4.71. The average of Mn concentrations in water varied from 0.434 ± 0.113 ppm in location 1, 0.390 ± 0.102 ppm in location 2, and 0.626 ± 0.296 ppm in location 3 and average of Mn concentrations in sediment varied from 41.906 ± 11.829 ppm in location 1, while 44.215 ± 4.286 ppm in location 2 and 62.483 ± 6.189 ppm in location 3. When comparing of Mn concentrations in three sampling point it was found that differences were not statistically significant (P>0.05) for water and were significant (P<0.05) for sediment.

The average of Mn concentrations in water varied in November 2010 to 0.284 ± 0.077 ppm, in March 2011 to 0.375 ± 0.047 ppm and in July 2011 to 0.220 ± 0.146 ppm, in July 2012 to 0.613 ± 0.230 ppm, in September 2012 to 0.861 ± 0.413 ppm, in October 2012 0.653 ± 0.313 ppm, and November 2012 to 0.376 ± 0.015 ppm. Average of
Mn concentrations in sediment varied in November 2010 to 44.233 ± 17.888 ppm, in March 2011 to 48.952 ± 6.116 ppm and July 2011 to 55.412 ± 11.228 ppm. After comparing of Mn concentrations during 7 times in a year, it was found that the differences were not significant (P>0.05) for sediment and water.



Figure 4.70 Mn concentrations in sediment of three sampling stations of Tunggak River during November 2010 until July 2011



Figure 4.71 Mn concentrations in water of three sampling stations of Tunggak River during November 2010 until November 2012

4. Ferrum

The distribution of Fe concentrations in water and sediment at three sampling points are showed in Figure 4.72 and 4.73. The average of Fe concentrations in water varied from 3.434 ± 1.960 ppm in location 1, 5.536 ± 3.916 ppm in location 2, and 9.329 ± 2.114 ppm in location 3 and average of Fe concentrations in sediment varied from 5103.508 ± 424.151 ppm in location 1, while 6387.386 ± 830.407 ppm in location 2 and 7031.546 ± 149.158 ppm in location 3. When comparing of Fe concentrations in three sampling point it was found that differences were not statistically significant (P>0.05) for water and were statistically significant (P<0.05) for sediment.

The average of Fe concentrations in water varied in November 2010 to 4.733 ± 2.672 ppm, in March 2011 to 9.593 ± 6.378 ppm, in July 2011 to 7.753 ± 5.021 ppm, in July 2012 to 5.664 ± 1.489 ppm, in September 2012 to 6.164 ± 1.956 ppm, in October 2012 to 4.192 ± 0.194 ppm, and November 2012 to 4.499 ± 0.479 ppm. Average

of Fe concentrations in sediment varied in November 2010 to 5884.886 ± 1232.425 ppm, in March 2011 to 6208.461 ± 789.538 ppm and July 2011 to 6429.093 ± 1189.547 ppm. After comparing of Fe concentrations during 7 times in a year, it was found that the differences were not significant (P>0.05) for sediment and water.



Figure 4.72 Fe concentrations in sediment of three sampling stations of Tunggak River during November 2010 until July 2011



Figure 4.73 Fe concentrations in water of three sampling stations of Tunggak River during November 2010 until November 2012

5. Nickel

The distribution of Ni concentrations in water and sediment at three sampling points are shown in Figure 4.74 and 4.75. The average of Ni concentrations in water varied from 0.069 ± 0.018 ppm in location 1, 0.064 ± 0.019 ppm in location 2, and 0.070 ± 0.016 ppm in location 3 and average of Ni concentrations in sediment varied from 2.849 ± 0.313 ppm in location 1, while 6.035 ± 2.019 ppm in location 2 and 6.938 ± 3.080 ppm in location 3. When comparing of Ni concentrations in three sampling point it was found that differences were statistically significant (P<0.05) for water and differences were not significant (P>0.05) for sediment.

The average of Ni concentrations in water varied in November 2010 to 0.014 ± 0.006 ppm, in March 2011 to 0.044 ± 0.001 ppm and in July 2011 to 0.034 ± 0.022 ppm, in July 2012 to 0.139 ± 0.043 ppm, in September to 0.073 ± 0.053 ppm, in October

2012 to 0.068 ± 0.012 ppm, and in November 2012 to 0.103 ± 0.013 ppm. Average of Ni concentrations in sediment varied in November 2010 to 4.001 ± 1.727 ppm, in March 2011 to 4.847 ± 2.381 ppm and July 2011 to 6.974 ± 3.436 ppm. After comparing of Ni concentrations during 7 times in a year, it was found that the differences were not statistically significant (P>0.05) for sediment and were significant (P<0.05) for water.



Figure 4.74 Ni concentrations in sediment of three sampling stations of Tunggak River during November 2010 until July 2011



Figure 4.75 Ni concentrations in water of three sampling stations of Tunggak River during November 2010 until November 2012

6. Cupper

The distribution of Cu concentrations in water and sediment at three sampling points are shown in Figure 4.76 and 4.77. The average of Cu concentrations in water varied from 0.084 ± 0.023 ppm in location 1, 0.105 ± 0.047 ppm in location 2, and 0.267 ± 0.053 ppm in location 3. Average of Cu concentrations in sediment varied from 2.629±0.364 ppm in location 1, while 3.540 ± 0.883 ppm in location 2 and 6.875 ± 1.185 ppm in location 3. When comparing of Cu concentrations in three sampling point it was found that differences were significant (P<0.05) for water and sediment.

The average of Cu concentrations in water varied in November 2010 to 0.009 ± 0.010 ppm, in March 2011 to 0.174 ± 0.003 ppm, in July 2011 to 0.120 ± 0.049 ppm, in July 2012 to 0.072 ± 0.052 ppm, in September 2012 to 0.085 ± 0.044 ppm, in October to 0.054 ± 0.011 ppm and in November 2012 to 0.105 ± 0.008 ppm. Average of

Cu concentrations in sediment varied in November 2010 to 3.830 ± 2.269 ppm, in March 2011 to 4.075 ± 1.816 ppm and July 2011 to 5.140 ± 2.722 ppm. After comparing Cu concentrations during 7 times in a year, it was found that the differences were not statistically significant (P>0.05) for sediment and were significant (P<0.05) for water.



Figure 4.76 Cu concentrations in sediment of three sampling stations of Tunggak River during November 2010 until July 2011



Figure 4.77 Cu concentrations in water of three sampling stations of Tunggak River during November 2010 until November 2012

7. Zinc

The distribution of Zn concentrations in water and sediment at three sampling points are shown in Figure 4.78 and 4.79. The average of Zn concentrations in water varied from 0.332 ± 0.070 ppm in location 1, 0.975 ± 0.086 ppm in location 2, and 1.263 ± 0.147 ppm in location 3 and average of Zn concentrations in sediment varied from 26.394 ± 8.022 ppm in location 1, while 33.893 ± 7.980 ppm in location 2 and 72.419 ± 8.091 ppm in location 3. When comparing of Zn concentrations in three sampling point it was found that differences were not statistically significant (P>0.05) for water and were significant (P<0.05) sediment.

The average of Zn concentrations in water varied in November 2010 to 0.129 ± 0.037 ppm, in March 2011 to 1.847 ± 1.608 ppm, in July 2011 to 0.535 ± 0.210 ppm, in July 2012 to 0.441 ± 0.095 ppm, in September 2012 to 1.006 ± 0.031 ppm, in

October 2012 to 1.503 ± 0.062 ppm and in November 2012 to 0.536 ± 0.015 ppm. Average of Zn concentrations in sediment varied in November 2010 to 36.590 ± 23.745 ppm, in March 2011 to 43.693 ± 26.423 ppm and July 2011 to 52.424 ± 23.921 ppm. After comparing of Zn concentrations during 7 times in a year, it was found that the differences were not significant (P>0.05) for sediment and water.



Figure 4.78 Zn concentrations in sediment of three sampling stations of Tunggak River during November 2010 until July 2011



Figure 4.79 Zn concentrations in water of three sampling stations of Tunggak River during November 2010 until November 2012

8. Arsenic

The distribution of As concentrations in water and sediment at three sampling points are shown in Figure 4.80 and 4.81. The average of As concentrations in water varied from 0.155 ± 0.034 ppm in location 1, 0.222 ± 0.017 ppm in location 2, and 0.291 ± 0.053 ppm in location 3 and average of As concentrations in sediment varied from 2.500 ± 0.546 ppm in location 1, while 1.828 ± 0.868 ppm in location 2 and 1.602 ± 0.331 ppm in location 3. When comparing of As concentrations in three sampling point it was found that differences were not significant (P<0.05) for water and sediment.

The average of As concentrations in water varied in November 2010 to 0.011 ± 0.003 ppm, in March 2011 to 0.248 ± 0.036 ppm, in July 2011 to 0.095 ± 0.071 ppm, in July 2012 to 0.474 ± 0.004 ppm, in September 2012 to 0.217 ± 0.082 ppm, in

October 2012 to 0.201 ± 0.014 ppm, and in November 2012 to 0.332 ± 0.071 ppm. Average of As concentrations in sediment varied in November 2010 to 1.420 ± 0.522 ppm, in March 2011 to 2.136 ± 0.826 ppm and July 2011 to 2.373 ± 0.350 ppm. After comparing of As concentrations during 7 times in a year, it was found that the differences were not significant (P>0.05) for sediment and were significant (P<0.05) for water.



Figure 4.80 As concentrations in sediment of three sampling stations of Tunggak River during November 2010 until July 2011



Figure 4.81 As concentrations in water of three sampling stations of Tunggak River during November 2010 until November 2012

9. Cadmium

The distribution of Cd concentrations in water and sediment at three sampling points are shown in Figure 4.82 and 4.83. The average of Cd concentrations in water varied from 0.062 ± 0.031 ppm in location 1, 0.008 ± 0.003 ppm in location 2, and 0.064 ± 0.012 ppm in location 3 and average of Cd concentrations in sediment varied from 0.134 ± 0.103 ppm in location 1, while 0.150 ± 0.018 ppm in location 2 and 0.148 ± 0.036 ppm in location 3. When comparing of Cd concentrations in three sampling point it was found that differences were not significant (P>0.05) for water and sediment.

The average of Cd concentrations in water varied in November 2010 to 0.003 ± 0.002 ppm, in March 2011 to 0.096 ± 0.075 ppm, in July 2011to 0.038 ± 0.032 ppm, in July 2012 to 0.036 ± 0.001 ppm, in September 2012 to 0.043 ± 0.004 ppm, in

October 2012 to 0.035 ± 0.015 ppm and in November 2012 to 0.052 ± 0.006 ppm. Average of Cd concentrations in sediment varied in November 2010 to 0.089 ± 0.058 ppm, in March 2011 to 0.151 ± 0.003 ppm and July 2011 to 0.207 ± 0.034 ppm. After comparing of Cd concentrations during 7 times in a year, it was found that the differences were not significant (P>0.05) for sediment and water.



Figure 4.82 Cd concentrations in sediment of three sampling stations of Tunggak River during November 2010 until July 2011



Figure 4.83 Cd concentrations in water of three sampling stations of Tunggak River during November 2010 until November 2012

10. Plumbum

The distribution of Pb concentrations in water and sediment at three sampling points are shown in Figure 4.84 and 4.85. The average of Pb concentrations in water varied from 0.539 ± 0.126 ppm in location 1, 0.343 ± 0.094 ppm in location 2, and 0.659 ± 0.033 ppm in location 3 and average of Pb concentrations in sediment varied from 6.384 ± 1.567 ppm in location 1, while 4.583 ± 2.197 ppm in location 2 and 7.592 ± 2.866 ppm in location 3. When comparing of Pb concentrations in three sampling point it was found that differences were not statistically significant (P>0.05) for water and differences were significant (P<0.05) for sediment.

The average Pb concentrations in water varied in November 2010 to 0.043 ± 0.002 ppm, in March 2011 to 0.116 ± 0.040 ppm, in July 2011 to 0.150 ± 0.080 ppm, in July 2012 to 0.211 ± 0.072 ppm, in September 2012 to 0.280 ± 0.095 ppm, in

October 2012 to 1.501 ± 0.336 ppm, in November 2012 to 1.745 ± 0.677 ppm. Average Pb concentrations in sediment varied in November 2010 to 5.769 ± 4.311 ppm, in March 2011 to 5.805 ± 1.459 ppm and July 2011 to 6.984 ± 0.477 ppm. After comparing of Pb concentrations during 7 times in a year, it was found that the differences were not significant (P>0.05) for sediment and water.



Figure 4.84 Pb concentrations in sediment of three sampling stations of Tunggak River during November 2010 until July 2011



Figure 4.85 Pb concentrations in sediment of three sampling stations of Tunggak River during November 2010 until November 2012

When comparing Al, Cr, Mn, Fe, Zn Cd and Pb concentrations in water at three sampling stations in Tunggak River, it was found that elements were not statistical significant (P>0.05) except Ni, Cu and As were statistical significantly different between sampling point in Tunggak river. When comparing Al, Cr, Mn, Fe, Cu, Zn, As and Pb concentrations in sediment at three sampling stations in Tunggak river it was found that elements were statistical significant (P>0.05) except Cd and Ni were not significant different between sampling point in Tunggak river.

Generally, the concentration of heavy metals in sediments Tunggak river very influence of human activity in this location because heavy metals entering natural waters become part of the water sediment system, and their distribution processes are controlled by a dynamic set of physical and chemical interactions and equilibria (Jain 2004; Vukociv *et al.*, 2011). As we know that rivers are dominant pathways for metals, and heavy metals become the significant pollutants of riverine systems (Dassenakis *et al.*, 2009). The behavior of metals in natural waters is a function of the substrate

sediment compositions. The suspended sediments composition, and the water chemistry (Mohiudin *et al.*, 2011), while location not significant influence concentration heavy metal in water due to of high-flow rate in these rivers. Zhang *et al.*, 2009 revealed that concentrations of Pb and Cu in water have no correlation with those in soil due to the persistently flow of water in Hengshuihu wetland and usually contain very low concentrations of contaminants (sometimes below detection limits) making identification of pollution events a difficult task (Allan *et al.*, 2006).

Sediments are preferred monitoring tools, since contaminant concentrations are orders of magnitude higher than in water, and they show less variation in time and space, allowing more consistent assessment of spatial and temporal contamination (Thorton and webb, 1979; Howart and Thornton, 1983; Turner *et al.*, 2001; Caccia *et al.*, 2003). Evidence of pollutant's transfer from urban wastewater, small-big industrial effluent, atmospheric emissions and domestic waste disposal to the sediment compartment have been found in the study area.

Sediment sample more effective in giving information about history of the pollution in the area compare to the water sample. This result may be due to decrease the water current in these locations (low tide or slow flow rate water river) that causes increase chemical interactions between metals and sediment such as: suspended solid absorption, surface sediment sorption and rate of re-deposition and the other may be results from the mixture of land runoff and untreated/treated wastewater from industry, which caused an increase level of heavy metal concentrations.

Moreover, as well known that metals can be adsorbed from the water body into/on fine particles surface and then dwell and move subsequently towards sediment particles. In the bottom sediments, the distribution of heavy metals is affected by mineralogical and chemical composition of suspended material, anthropogenic influences, and in-situ processes such as deposition, sorption, and enrichment in an organism (Fortsner and Muller, 1975, Jain *et al.*, 2005; Shakeri and Moore, 2010). Toxicity of sediment due to particularly surfaces at sediments, may serve as a metal pool that can release heavy metals process, causing potential adverse health effects to

the ecosystems because of their serious toxicity and persistence (Howard and Nombela, 2003; McCready *et al.*, 2006; Valdes *et al.*, 2010). In this study, much higher concentrations of Al in sediment were found that those of other heavy metals. During the sample collections in the field, it was observed that the wastewater discharge from activity industry and disposal domestic waste through big sewage to channel contacting river. Many kinds of the old material results of chemical industry, batteries, iron, plastic, and, etc., were stored. It is not surprising as well with the highest concentrations of Al and Fe in water and sediment found in the study.

Cd concentration in sediment samples is lowest among ten heavy metals. The result is similar to the study of Ghrefat *et al.*, 2010 about concentrations of Cd in Kafrain Dam ranked three of five studies, with average concentrations of Cd obtained was lower than that of Pulicat Lake, India (Kamala-Kannan *et al.*, 2007) and the Seyhan Dam (Cevik *et al.*, 2009). The concentration's Cd in sediment lowest other Al, As, Cu, Cr, and Zn mainly 0.79 ± 0.14 otherwise water and sediments of River, which flows through the industrial and commercial areas of Kumasi in the Ashanti region of Ghana (Adomako *et al.*, 2008). Nevertheless, none of the industrial plants of that area use cadmium in their daily processes. Besides, it is more concentrated in the sediments from the upstream Tunggak River near the factory. Notwithstanding, in the other sites, the content is Cd that presented in lower concentration in the intertidal sediments. These could mean that this metal has different sources within the river system. Keeping in mind that this metal is highly toxic even at low concentrations, its accumulation within tidal flat sediments may be largely important as they can act as a metal reservoir, and so a potential of Cd source for the estuary.

However, upstream Tunggak river sediments more influenced by chipboard and chemical industry can also act as an important sink at first and then the source to the surrounding environment. It can be observed that water circulation of river may affect the heavy metal accumulation in both water and sediments.

In this study, concentrations of heavy metal accumulated in sediment higher than accumulated in water, due to water mass characteristics are continually changing (e.g. water renewal, dilution process, etc.) and usually contain very low concentrations of contaminants (sometimes below detection limits) making identification of pollution events a difficult task (Allan *et al.*, 2006). Nevertheless, sediments are known to act as sink and reservoir for wide-range pollutants, including heavy metals (Morrillo *et al.*, 2007), reaching higher concentrations than it the water column, which makes measurement easier. However, heavy metals could accumulate in sediments of water bodies therefore the concentrations will always increase (Begum et al., 2009).

Whereas in water, heavy metals tended to distribute along the flows and there are diluting effects so the concentrations could be lower. An increment tendency of heavy metals in sediments could be due to a high concentration in water as well. Their distribution is controlled by a dynamic set of physical-chemical interaction and equilibria, largely governed by pH, concentration and type of ligands and chelating agents, oxidation state of the mineral components and the redox conditions of the systems (Singh et al., 2005).

Furthermore, sediments contain a historical pollution input record that allows chronological contamination studies (Cundy *et al.*, 2003). Therefore, the result of the present study showed that the heavy-metal concentrations accumulate in sediments can represent the activities available in the area and are likely to increase with growing industrial, agricultural, population, and, etc.

4.18 Relationship element in Location 1

The location 1 of Tunggak River has received untreated/treatment wastewater from the where small-medium industries, wet markets and established residents located from upstream. The Pearson correlation coefficients of the heavy metals in water and sediment samples at this location 1 are depicted in Table 4.34.

А.	Al	Cr	Mn	Fe	Ni	Cu	Zn	As	Cd	Pb
Al	1									
Cr	-0.101	1								
Mn	0.435	0.256	1							
Fe	0.767*	-0.296	0.492	1						
Ni	0.058	-0.404	0.195	0.346	1					
Cu	-0.153	0.190	0.244	-0.010	0.553	1				
Zn	-0.010	0.813**	0.628	-0.073	-0.060	0.338	1			
As	0.207	0.525	0.094	0.067	-0.230	-0.288	0.209	1		
Cd	0.393	-0.308	0.704*	0.427	0.068	-0.165	0.158	-0.315	1	
Pb	0.434	0.534	0.530	0.475	0.296	0.336	0.711*	0.314	0.011	1
	A 1	0	M	E	NT'	C	7		01	
в.	AI	Cr	Mn	Fe	N1	Cu	Zn	As	Cđ	Pb
Al	1									
Cr	0.543	1								
Mn	0.772**	0.439	1							
Fe	0.340	0.677**	0.357	1						
Ni	0.451	0.490	0.073	0.024	1					
Cu	0.802*	0.895**	0.562*	0.666*	0.551	1				
Zn	0.117	0.236	0.236	-0.217	-0.274	-0.249	1			
As	0.502*	0.623	0.719**	0.451	0.367	0.724*	0.267	1		
Cd	0.831**	0.938**	0.708*	0.451	0.601	0.602*	0.279	0.808**	1	
Pb	0.774*	0.465	0.289	-0.482	0.713*	0.256	0.476	0.568	0.662	1
*. Co	*. Correlation is significant at the 0.05 level (2-tailed).									
** Correlation is significant at the 0.01 level (2-tailed)										

Table 4.34. Correlation matrix of levels of heavy metals in riverine sediment and water samples location 1

. Correlation is signifi level (2--tailed).

A : Sediment sample

B : Water sample

From Table 4.34, there are strong positive correlation coefficients between the elements in river sediments and the correlation between elements in the sediments sample is shown in Table 4.35 Meanwhile in Table 4.36, it shows the correlation between elements in the water sample

Pairs of elements	Coefficients
Al-Fe	0.767*
Cr-Zn	0.813*
Mn-Cd	0.704*
Zn-Pb	0.711*

Table 4.35 Pairs of element correlation elements in sediment

*. Correlation is significant at the 0.05 level (2-tailed). **. Correlation is significant at the 0.01 level (2-tailed

Elements in river water samples showed strong negative correlation coefficients between themselves as follows Table 4.36.

Pairs of elements	Coeficient		
Al-Mn	0.772**		
Al-Cu	0.802*		
Al-As	0.504*		
Cd-Al	0.831**		
Pb-Al	0.774**		
Fe-Cr	0.677**		
Cr-Cu	0.895**		
Cd-Cr	0.938**		
Mn-Cu	0.562*		
As-Mn	0.719*		
Cd-Mn	0.708*		
Cu-Fe	0.666*		
Cu-As	0.724**		
Cu-Cd	0.602*		

Table 4.36 Pairs of correlation element in water

*. Correlation is significant at the 0.05 level (2-tailed). **. Correlation is significant at the 0.01 level (2-tailed Positive correlations between heavy metals indication same sources pollution and common pollution in this area.

Element	Correlation Coefficients			
Al	0.684			
Cr	-0.845*			
Mn	-0.302			
Fe	0.863**			
Ni	0.359			
Cu	-0.041			
Zn	0.451			
As	0.469			
Cd	0.296			
Pb	0.604*			

Table 4.37 Pearson's correlation element in water-sediment location 1

*. Correlation is significant at the 0.05 level (2-tailed). **. Correlation is significant at the 0.01 level (2-tailed).

From Table 4.34 and Table 4.35, it is clearly shows that these metals are associated with each other, and the relationship does exist between the variables. It is indicates that metals in water and sediment in location 1 of Balok River have same sources pollution from anthropogenic. This is due to at the upstream of location 1, there are so many human activities such as residential, wet market, traffic highway and small industry that always produce wastewater every day and discharge to Tunggak River.

From Table 4.37, Fe and Pb concentrations between water and sediment show positively significant correlation while Fe concentration shows the highest significant correlation with coefficient value of 0.863 at the 0.01 level (Table 4.37). While for Cr concentration shows the negative significant correlation. There is no positively significant correlation Al, Ni, As and Cd concentration and there is no negatively significant correlation Mn, Cu and Zn. This is indication weak correlation between water and sediment due to flow rate, purity water, and change condition environment.

4.19. Relationship element in Location 2

In this location receive wastewater within the huge amount from domestic waste disposal, wastewater from pipe processing industries at the upstream and, etc. Therefore, correlation between heavy metal accumulated in water and sediment need to know commonly of pollution and interaction between heavy metal in water and sediment. Pearson's correlation interrelationships heavy metals at location 2 Tunggak River shown in Table 4.38.

 Table 4.38. Correlation matrix of levels of heavy metals in riverine sediment and water samples location 2

А.	Al	Cr	Mn	Fe	Ni	Cu	Zn	As	Cd	Pb
Al	1									
Cr	-0.331	1								
Mn	-0.423	0.439	1							
Fe	0.334	-0.459	0.227	1						
Ni	0.579*	-0.262	-0.226	0.28	1					
Cu	0.176	0.338	0.640	0.470	-0.008	1				
Zn	0.207	-0.362	0.497	0.789*	0.009	0.518	1			
As	0.201	0.069	0.244	0.010	0.176	0.417	0.380	1		
Cd	-0.136	0.337	0.412	0.043	0.403	0.211	-0.081	0.157	1	
Pb	-0.097	-0.485	0.506*	0.608*	0.164	0.281	0.807**	0.416	0.145	1
D	A 1	Cr	Mn	Fa	Ni	Cu	7n	A a	Cd	Dh
D .		CI	IVIII	Te	111	Cu	ZII	Að	Cu	ru
AI	1			11.0	71 L-					
Cr	0.823**	1								
Mn	-0.415	0.233	1							
Fe	-0.418	0.645	0.808	1						
Ni	0.625*	0.815*	0.510*	-0.461	1					
Cu	0.656*	0.445	-0.190	0.107	0.120	1				
Zn	0.389	0.672**	-0.054	-0.352	0.458	0.637*	1			
As	0.774**	0.553	-0.453	-0.602	0.557	0.556	0.711**	1		
Cd	0.667*	0.517	-0.402	-0.178	0.122	0.681*	0.641**	0.637 *	1	
Pb	0.123	-0.077	-0.386	-0.423	0.362	-0.142	0.128	0.156	0.018	1

*. Correlation is significant at the 0.05 level (2-tailed).

**. Correlation is significant at the 0.01 level (2-tailed).

A : Sediment sample

B : Water sample

There are strong positive correlation coefficients between the elements in river sediments as follows Table 4.39.

Pairs of elements	Coefficient				
Fe-Zn	0.789*				
Zn-Pb	0.807**				
Fe-Pb	0.608*				
Mn-Pb	0.506*				
Al-Ni	0.579*				

Table 4.39. Pairs of element correlation in sediment sample

**. Correlation is significant at the 0.01 level (2-tailed).

*. Correlation is significant at the 0.05 level (2-tailed).

Elements in river water samples showed strong negative correlation coefficients between themselves as follows Table 4.40. There is no negatively correlation in each pair element in water and sediment.

Pairs of elements	Coefficient
Al-Cr	0.823**
Al-Cu	0.656*
Al-Ni	0.625*
Al-As	0.774**
Al-Cd	0.667*
Cr-Ni	0.815**
Cr-Zn	0.672**
Mn-Ni	0.510*
Zn-Cu	0.637*
Cd-Cu	0.681*
As-Zn	0.711
Cd-Zn	0.641**
As-Cd	0.637

Table 4.40. Pairs of element correlation in water sample

**. Correlation is significant at the 0.01 level (2-tailed).

*. Correlation is significant at the 0.05 level (2-tailed).

Element	Correlation Coefficients				
Al	-0.541				
Cr	0.814*				
Mn	-0.549*				
Fe	-0.619*				
Ni	-0.410				
Cu	-0.612*				
Zn	0.553				
As	0.718*				
Cd	0.009				
Pb	0.159				

Table 4.41 Pearson's correlation of element in water-sediment location 2

**. Correlation is significant at the 0.01 level (2-tailed). *. Correlation is significant at the 0.05 level (2-tailed).

For Cr, and As concentrations between water and sediment show positively significant correlation while Cr concentration shows the highest significant correlation with coefficient value of 0.814 at the 0.05 level (Table 4.41). While for Mn, Fe and Cu concentration shows the negative significant correlation while Fe concentration shows the highest significant correlations with coefficient value of 0.619. There is no positively significant correlation Cd, Zn and Pb concentration and there is no negatively significant correlation Al and Ni.

4.20. Relationship element in Location 3

In this location receive wastewater within the huge amount from pipe production of chemical industry, chipboard industry, market, and some residential. Therefore, correlation between heavy metal accumulated in water and sediment needed to know commonly of pollution and interaction between heavy metal in water and sediment. Pearson's correlation interrelationship heavy metal at location 3 Tunggak River shown in Table 4.42.

А.	Al	Cr	Mn	Fe	Ni	Cu	Zn	As	Cd	Pb
Al	1									
Cr	0.272	1								
Mn	0.383	0.094	1							
Fe	0.562*	-0.142	0.06	1						
Ni	0.163	-0.062	-0.084	-0.326	1					
Cu	0.18	0.342	0.253	-0.374	-0.014	1				
Zn	0.455	0.204	-0.065	-0.104	0.850**	0.231	1			
As	-0.021	0.218	-0.071	-0.365	0.186	0.860**	0.349	1		
Cd	-0.569*	-0.055	-0.138	-0.951**	0.496	0.273	0.262	0.333	1	
Pb	0.072	0.024	0.402	0.293	<mark>-0.4</mark> 40*	-0.129	-0.456*	-0.252	-0.409)* 1
	A 1	Cr	Ma	Ee	NE	Cu	7	Ac	Cł	Dh
D.	AI	Cr	IVIII	ге	INI	Cu	ZII	As	Cu	PO
Al	1									
Cr Ma	0.712**	1								
Nin E	0.151	0.319	1							
Fe	0.576**	0.417	0.419	1						
N1	0.209	0.682*	-0.268	0.481	1					
Cu	0.722*	0.511	0.293	0.648*	0.221	1				
Zn	0.809**	0.633**	0.062	0.514	0.174	0.407	1			
As	0.813*	0.439	0.574*	0.744**	0.483	0.317	0.542*	1		
Cd	0.438	0.684*	0.274	0.275	0.672*	0.651*	0.494	0.741**	1	
Pb	0.519	0.357	0.337	0.399	-0.431	0.773*	0.204	0.353	0.082	1
* Co	* Correlation is significant at the 0.05 level (2-tailed)									

Table 4.42 Correlation matrix of levels of heavy metals in riverine sediment and water samples location 3

elation is signi

**. Correlation is significant at the 0.01 level (2-tailed).

A : Sediment sample

B : Water sample

There are negative correlation coefficients between the elements in river sediments as follows Table 4.43.

Table 4.43. Pairs of correlation element in sediment sample

Pairs of elements	Coefficients
Al-Fe	0.562*
Zn-Ni	0.850**
As- Cu	0.860*
Al-Cd	-0.569*
Fe-Cd	-0.951**
Ni-Pb	-0.440*
Cd-Pb	-0.409*

*. Correlation is significant at the 0.05 level (2-tailed).

**. Correlation is significant at the 0.01 level (2-tailed

Negative and inverse correlations between metals indicate that these metals are derived from different sources and that this metals is not associated with other metals (Ghrefat *et al.*, 2010). Elements in river water samples showed strong positive correlation coefficients between themselves as follows Table 4.44.

Pairs of elements	Coefficients
Al-Cr	0.712**
Al-Fe	0.576**
Al-Cu	0.722*
Al-Zn	0.809**
Al-As	0.813*
Al-Ni	0.682**
Cr-Zn	0.633*
Cr-Cd	0.684**
Mn-As	0.7574*
Fe-Cu	0.648*
Ni-Cd	0.672*
Cu-Cd	0.651*
Cu-Pb	0.773*
Zn-Cd	0.542*
As-Cd	0.741**

Table 4.44. Pairs of correlation element in water

*. Correlation is significant at the 0.05 level (2-tailed). **. Correlation is significant at the 0.01 level (2-tailed

There is no negatively correlation coefficient in water. Positive correlations between heavy metal concentrations suggested either a common or a similar geochemical behavior origin (Kucuksezgin *et al.*, 2006). Al and Fe as well know lithogenic elements (Mico *et al.*, 2006) due to Al being one of the most abundant element on the earth while Fe is also an abundant element in the structure of clay minerals and is also associated with particles surface as oxide coatings (Yap *et al.*, 2011). Better correlation of Cu, Cd, As, Pb, and Zn with Fe/Al, a major component of clay minerals, indicate a natural origin of the metals, as shown with sediments of location 3 Tunggak River that suggests common pollution sources coming from industrial park.

Element	Correlation Coefficients			
Al	-0.808**			
Cr	-0.711**			
Mn	0.815**			
Fe	0.754*			
Ni	0.402			
Cu	0.568*			
Zn	0.196			
As	-0.529*			
Cd	0.244			
Pb	-0.593*			

Table 4.45. Pearson's correlation element in water and sediment

**. Correlation is significant at the 0.01 level (2-tailed). *. Correlation is significant at the 0.05 level (2-tailed).

From Table 4.45, Mn, Fe, and Cu, concentrations between water and sediment show positively significant correlation while Mn concentration shows the highest significant correlation with coefficient value of 0.815 at the 0.05 level. For Al, Cr, As, and Pb concentration shows the negative significant correlation while Al concentration shows the highest significant correlations with coefficient value of -0.808 at the 0.05 level. There is no positively significant correlation Ni, Zn and Cd accumulated in water. From table above values suggest a fairly strong relationship between water and sediment elements concentrations in location 3 Tunggak River. It can be inferred that water current aided in the interactions between water column and bed sediments. The good positive correlation between elements concentrations in water and sediments indicates a possible action of sediments as a secondary pollution source. Four negative correlations were recorded between Al, Cr, As, and Pb between sediment and water. This suggests that there are different sources anthropogenic.

4.21. Principal Component Analysis (PCA) on sediment location 1 Tunggak River

Principal component analysis has been carried out on the raw data (Appendix A9) of total heavy metals accumulated in sediment. Factors with Eigenvalues greater than 1 were taken into account. Three principal components (PCs) were extracted,

together, explaining 77.165% of total variance in the data. Variable loading coefficients of the three principal components are listed in Table 4.46. The graphic representation of three components is also shown in Figure 4.86. The first component (PC1) explained 33.190% of the total variance with an Eigenvalue of 3.319 and dominated by Zn, Cr, and Pb, registered factor loadings greater than 0.5 mainly 0.928, 0.897, and 0.800, respectively. This component can be termed "anthropogenic activity" due to Zn, Cr, Pb and Mn was related to human activities in other works (Uria et al., 2009). Sorme et al., 2002 identified domestics' construction and car related sources and untreated wastewater as the main sources of Zn. Probable sources of the pollutant in location 1 might be the industrial discharges, municipal waste water, household garbage and urban runoff Kampung seberang balok. Although Mn and Pb are also commonly present in municipal wastewaters, industrial effluents, and atmospheric emissions, distribution patterns were not associated with main sources identified in urban area (Gonzales et al., 2011). Cd present in environment, the origin varies between different areas of the region depending on specific human activities that are locally relevant (Mico et al., 2006) like chemical industry, fertilizer, and municipal domestic waste. In addition, heavy metals from an anthropogenic source could be more mobile than lithogenic metals according to (Burt et al., 2003). This could constitute a threat to human health through the food web and should be investigated in this area study, due to near location 1 there is fish raising pond and live some crab that sometimes people catches for sell or consumption.

The second component (PC2) explained 25.840% of the total variance with eigenvalue of 2.584% and high values of Fe, Al, Cd and Mn recorded absolute factor loading greater than 0.5 were 0.889, 0.846, 0.732 and 0.667, respectively. This component can be termed "natural factor" due to Fe, Al and Mn as well-known lithogenic element (Mico *et al.*, 2006) whereas the present of Cd seemed to also influence lithogenic.

Heavy Metal		Component			
		PC1	PC2	PC3	
Zn		0.928			
Cr		0.897	-0.299	-0.296	
Pb		0.800	0.377	0.157	
Fe			0.889	0.103	
Al			0.846	-0.192	
Cd			0.732	0.101	
Mn		0.548	0.667	0.186	
Cu		0.397	-0.167	0.815	
Ni			0.236	0.812	
As		0.624		-0.458	
Eigenvalue		3.319	2.584	1.813	
% of Total Variance		33.190	25.840	18.134	
Cumulative% of variance		33.190	59.031	77.165	

Table 4.46 Matrix of the principal component analysis loading of metals and major elements of river sediment in Tunggak River.^{ab}

^a Extraction Method: Principal Component Analysis; Rotation Method: Varimax with Kaisar Normalization.; Rotation converged in 6 iterations.

^b The boldfaced numbers are the dominant elements in different PCs



Component Plot in Rotated Space

Figure 4.86 Plot of loading PCA location 1 sediment in Tunggak River

The third PC, accounting for 18.13% of the total variance with an Eigenvalues 1.813%, was weighted only Ni, and Cu, was positive correlated factor loading greater than 0.5 were 0.815 and 0.812, respectively. This component can be termed "natural

factor' due to this component influence lithogenic elements. Based on (Boyle, 1981), that Nickel can enter surface waters from natural sources such as particulate matter in rainwater, through the dissolution of bedrock minerals and soil phases. It may also be deposited in the sediment by precipitation, complexation and adsorption on clay particles, and via uptake by biota. Cu may be related with slurry application this indicating a combined origin (lithogenic and anthropogenic) for this metal (Uria *et al.,* 2009), addition Ni was as well known lithogenic elements (Mico *et al.,* 2006). Within this region, it seems clear that Ni, and Cu have a lithogenic origin, since these metals are in general present in the parent material in soil. The pasture soils were sited in a river basin, and thus this is considered an alluvial-coalluvial area (Uria *et al.,* 2009).

4.22. Principal Component Analysis (PCA) on water in location 1 Tunggak River

Three principal components (PCs) were extracted, together, explaining 89.632% of total variance in the data. Variable loading coefficients of the three principle components are listed in Table 4.47. The graphic representation of the three components is also shown in Figure 4.87.

Table 4.47 Matrix of the principal component analysis loading of metals and major elements of river water in Tunggak River.^{a,b}

Heavy Metal	Component			
	PC1	PC2	PC3	
Cr	0.804	0.438		
As	0.781	0.345		
Mn	0.638		0.431	
Cd	0.808	0.618		
Cu	0.728	0.258	0.378	
Fe	0.251	-0.105	-0.452	
Ni		0.884	0.221	
Pb	0.759	0.172	0.423	
Al	0.204	0.905		
Zn			0.753	
Eigenvalue	5.025	2.053	1.180	
% of Total Variance	50.252	20.532	11.852	
Cumulative% of variance	50.252	70.784	82.636	

^a Extraction Method: Principal Component Analysis; Rotation Method: Varimax with Kaisar Normalization.; Rotation converged in 5 iterations.

^b The boldfaced numbers are the dominant elements in different PCs

The first component (PC1) explained 50.252% of the total variance with an Eigenvalue of 5.025, dominated elements in this variable loading mainly Cr, As, Mn, Cd, Cu, and Pb registered factor loadings greater than 0.5 mainly 0.804, 0.781, 0.638, 0.808, 0.728 and 0.759, respectively. This component can be termed to "anthropogenic factor", probably due to this location at downstream, which receive wastewater discharges from that part of Population (Balok Makmur Resident and Kampung seberang Balok Resident) and untreatment or treatment wastewater industrial at upstream. The main sources of Lead in water are manufacturing industries, smelting, and refinery of metals, sewage sludge and domestic waste water (Fergusson, 1990). Copper can exist in aquatic environments in three broad categories: particulate, colloidal and sediments, and soluble. It sorbs rapidly to sediments, and its desorption into bulk water depends on pH, salinity, and presence of natural and/or synthetic chelating agents. Chromium released by the electroplating, steel manufacturing, leather tanning and textile industries is the main sources of contamination in water. While, Manganese and its compound can exist as solids in the sediments and as solutes or small particles in water (Baroso et al., 2009).





Figure 4.87 Plot of loading PCA location 1 water in Tunggak River

The second component (PC2) explained 20.532% of the total variance with eigenvalue of 2.053% and high values of Cd, Ni, and Al recorded absolute factor loading greater than 0.5 were 0.618, 0.884, and 0.905, respectively. This component can be termed "natural factor" due to Ni and Al were as well known lithogenic origin (Mico *et al.*, 2006), and (Rautengarten *et al.*, 1995) suggest that the Cd distribution is controlled by small mineral particles and organic matter, its mobility being determined mainly by clay content.

The third principal component (PC3), accounting for 11.852% of the total variance with Eigenvalue 1.1852, only correlated with Zn factor loading greater than 0.5 was 0.753. This component can be termed to "anthropogenic factor and natural factor" due to no relation with other metals in PC3. Zinc can have lithogenic sources as it forms a number of soluble salt (e.g., chlorides, sulphates and nitrates) or insoluble salts (e.g., silicates, carbonates, phosphates, oxides and sulphides) according to the prevailing pedogenic process (Adriano, 2001). However, Zn and its compounds are also used in different manufactures goods (e.g., paints, cosmetics, automobile tyres, and electrical apparatus) and in agricultural fertilizers. In the case of Zn, this element displays a combined relationship with both groups and seems to have both natural and anthropogenic origin (Mico *et al.*, 2006).

4.23. Principal Component Analysis (PCA) on sediment in location 2 Tunggak River

Principal component analysis has been carried out on the raw data of total heavy metals accumulated in water. Factors with Eigenvalues greater than 1 were taken into account. Three principal components (PCs) were extracted, together, explaining 74.942% of total variance in the data. Variable loading coefficients of the three principal components are listed in Table 4.48. The graphic representation of the three components is also shown in Figure 4.88.

Heavy Metal	Compone	nt	
	PC1	PC2	PC3
Zn	0.963	0.109	
Pb	0.879	0.134	
Fe	0.827		0.264
Cd	-0.116	0.754	0.184
Mn	0.427	0.694	-0.510
Cr	-0.515	0.673	-0.388
Cu	0.463	0.669	
As	0.312	0.486	0.197
Ni	/ /	0.212	0.888
Al	0.144		0.839
Eigenvalue	3.470	2.420	1.604
% of Total Variance	34.698	24.202	16.040
Cumulative% of variance	34.698	58.902	74.942

Table 4.48Matrix of the principal component analysis loading of metals and majorelements of river sediment in Tunggak River.

^a Extraction Method: Principal Component Analysis; Rotation Method: Varimax with Kaisar Normalization.; Rotation converged in 6 iterations.

^b The boldfaced numbers are the dominant elements in different PCs



Component Plot in Rotated Space

Figure 4.88 Plot of loading PCA location 2 sediment in Tunggak River

The first component (PC1) explained 34.698% of the total variance with an Eigenvalue of 3.469 and dominated by Zn, Pb, Fe and Cr, registered factor loadings

greater than 0.5 mainly 0.963, 0.879, and 0.827, respectively while Cr had absolute Eigenvalues less than -0.5 was -0.515. This component can be termed "anthropogenic activity" due to this element related to the human activity. It has been reported that Pb can form stable forms with Fe hydroxide and Mn dioxide (Ramos *et al.*, 1994 and Liu *et al.*, 2011), which has been proven to be sensitive to anthropogenic input (Modak *et al.*, 1992). This agreement wit result reported in Morillo *et al.*, 2004, which showed that Fe and Mn hydroxides are important scavengers of Pb in sediment.

The second component (PC2) explained 24.202% of the total variance with Eigenvalue of 2.420% and high values of Cd, Mn, Cr and Cu recorded absolute factor loading greater than 0.5 were 0.754, 0.694, 0.673 and 0.669, respectively. This component term to "anthropogenic factor" due to present of these heavy metals related with human activity. As mention above about activity in location 1 Tunggak River, there are many residential around Tunggak River and Chemical Industry area at upstream Tunggak River, could be considered as ones of the pollution sources. The third PC, accounting for 16.040% of the total variance with an Eigenvalues 1.604%, was weighted only Al and Ni, was positive correlated factor loading greater than 0.5 were 0.888 and 0.839, respectively, while Mn had absolute Eigenvalues less than -0.5 was -0.510. This component term to "natural factor" because concentrations of heavy metals seem to be controlled by parent rock composition. Otherwise, Ni is used metalfinishing, mining, and chemical industries (Aziz et al., 2008) that contribute anthropogenic pollution in sediment river but in relation with Al and Mn as well known lithogenic elements (Mico et al., 2006) of this group of these components therefore we can interpret as one of the natural element concentrations.

4.24. Principal Component Analysis (PCA) on water in location 2 Tunggak River

Three principal components (PCs) were extracted, together, explaining 84.614% of total variance in the data. Variable loading coefficients of the three principal components are listed in Table 4.49. The graphic representation of the three components also shown in Figure 4.89.

Heavy Metal		Сотро			
		PC1	PC2	PC3	
Zn		0.801		0.233	
Al		0.915	-0.253	0.253	
Cr		0.896	0.113	0.318	
Cu		0.716			
Cd		0.905		-0.12	
As		0.811	-0.324	0.383	
Fe		-0.107	0.901		
Pb			-0.800	0.111	
Mn		-0.179	0.750	0.461	
Ni		0.267		0.917	
Eigenvalue		4.705	2.4731	1.5701	
% of Total	Variance	47.052	24.731	15.701	
Cumulative	% of variance	47.052	71.783	87.484	

Table 4.49 Matrix of the principal component analysis loading of metals and major elements of river water in Tunggak River. ^{a,b}

^a Extraction Method: Principal Component Analysis; Rotation Method: Varimax with Kaisar Normalization.; Rotation converged in 5 iterations. ^b The boldfaced numbers are the dominant elements in different PCs



Component Plot in Rotated Space

Figure 4.89 Plot of loading PCA location 2 water in Tunggak River

The first component (PC1) explained 47.052% of the total variance with an Eigenvalue of 4.075 and dominated by Zn, Al, Cr, Cu, Cd, and As registered factor
loadings greater than 0.5 mainly 0.801, 0.896, 0.716, 0.716, 0.905, and 0.811, respectively. The second component (PC2) explained 24.731% of the total variance with Eigenvalue of 2.473% and high values of Fe and Mn recorded absolute factor loading greater than 0.5 were 0.901, and 0.750, respectively, while Pb had absolute Eigenvalues less than -0.5 was -0.800. The third PC, accounting for 15.701% of the total variance with an Eigenvalues 1.570%, was weighted only Ni was strong positive correlated factor loading greater than 0.5 were 0.917. Most nickel is used for the production of stainless steel and other nickel alloys with high corrosion and temperature resistance. Nickel can enter surface waters from natural sources such as particulate matter in rainwater, through the dissolution of bedrock minerals and soil phase (Boyle, 1981). It may also be deposited in the sediment by precipitations, complexation, and adsorption on clay particles and via uptake by biota. The release of nickel from sediments may occur as the result of microbial activity or changes in physical and chemical parameters such as pH, ionic strength and sorption process (Di Toro *et al.*, 1991).

4.25. Principal Component Analysis (PCA) on sediment in location 3 Tunggak River

Principal component analysis has been carried out on the raw data of total heavy metals accumulated in sediment. Factors with Eigenvalues greater than 1 were taken into account. Three principal components (PCs) were extracted, together, explaining 74.079% of total variance in the data. Variable loading coefficients of the three principal components are listed in Table 4.50. The graphic representation of three components is also shown in Figure 4.90. The first component (PC1) explained 33.708% of the total variance with an Eigenvalue of 3.3708 and dominated by Fe and Al, registered factor loadings greater than 0.5 mainly 0.872, and 0.757, respectively while Cd had absolute Eigenvalues less than -0.5 was -0.870. This term can be defined to "natural factor" due to Fe and Al related from lithogenic origin. While Cd commonly from anthropogenic but in this case include to natural factor due to lying in the same component with Al and Fe (lithogenic elements). Rautengarten *et al.*, 1995 suggest that the Cd distribution is controlled by small mineral particles and organic matter, its

mobility being determined mainly by clay content. In this case at location 3 tunggak river, Cd has mixed sources are lithogenic and anthropogenic sources.

Heavy Meta	al	Component		
		PC1	PC2	PC3
Fe		0.872	-0.172	-0.283
Cd		-0.870	0.358	0.131
Al		0.857	0.298	0.326
Zn		0.148	0.927	0.254
Ni		-0.111	0.912	
Pb		0.324	-0.671	
Cu		-0 .197		0.928
As		-0.326	0.231	0.750
Cr		0.141		0.585
Mn		0.342	-0.252	0.435
Eigenvalue		3.371	2.232	1.805
% of Total	Variance	33.708	22.32	18.048
Cumulative	% of variance	33.708	56.031	74.079

Table 4.50 Matrix of the principal component analysis loading of metals and major elements of river sediment in Tunggak River.^{ab}

^a Extraction Method: Principal Component Analysis; Rotation Method: Varimax with Kaisar Normalization.; Rotation converged in 5 iterations.

^b The boldfaced numbers are the dominant elements in different PCs



Component Plot in Rotated Space

Figure 4.90 Plot of loading PCA location 3 sediment in Tunggak River

The second component (PC2) explained 22.32% of the total variance with eigenvalue of 2.232% and high values of Zn and Ni recorded absolute factor loading greater than 0.5 were 0.927 and 0.912 respectively while Pb had absolute Eigenvalues less than -0.5 was -0.671. The third PC, accounting for 18.048% of the total variance with an Eigenvalues 1.805%, was weighted only Cu, As, and Cr, was positive correlated factor loading greater than 0.5 were 0.928, 0.750 and 0.585, respectively. Component 2 and 3 can be termed to "anthropogenic factor" due to related to human activity. At locations, 3 Tunggak River near Factory chipboard, highway, residential and small market that had untreatment/treatment wastewater discharge to the Tunggak River.

4.26. Principal Component Analysis (PCA) on water in location 3 Tunggak River

Principal component analysis has been carried out on the raw data (appendix A-11) of total heavy metals. Two principal components were obtained with Eigenvalues>1, explaining 75.898% of the total variance in water dataset. Variable loading coefficients of the two principal components are listed in Table 4.51. The graphic representation of the two components is also shown in Figure 4.91.

Table 4.51 Matrix of the principal component analysis loading of metals and major elements of river sediment in Tunggak River.^{a,b}

		the second se
Heavy Metal	Component	
	PC1	PC2
Cd	0.872	
Pb	0.911	0.152
Mn	0.828	0.341
Zn	0.841	
Cr	0.861	0.149
As	0.804	0.442
Cu	0.786	0.268
Ni	0.722	-0.547
Fe		0.859
Al	0.324	0.700
Eigenvalue	5.748	2.064
% of Total Variance	57.481	20.643
Cumulative% of variance	57.481	78.124

^a Extraction Method: Principal Component Analysis; Rotation Method: Varimax with Kaisar Normalization.; Rotation converged in 5 iterations.

^b The boldfaced numbers are the dominant elements in different PCs

Component Plot in Rotated Space



Figure 4.91 Plot of loading PCA location 3 water in Tunggak River

The first component (PC1) explained 57.481% of the total variance with an Eigenvalue of 5.748% and dominated by Cd, Pb, Mn, Zn, Cr, As, Cu and Ni, registered factor loadings greater than 0.5 mainly 0.872, 0.911, 0.828, 0.841, 0.861, 0.804, 0786 and 0.722, respectively. This term can be defined "anthropogenic factor" due to this element related human activity in urban area. The second component (PC2) explained 20.643% of the total variance with eigenvalue of 2.064% and high values of Fe and Al recorded absolute factor loading greater than 0.5 were 0.859 and 0.700, while Ni had absolute Eigenvalues less than -0.5 was -0.547. This component can be termed to "natural factor" due to lithogenic element very dominant in this component. However, in this case present of Ni indicated mixed sources are lithogenic and anthropogenic factors.

4.27. Quantification of stream sediments pollution Tunggak River

The Enrichment Factors (EF) for the streams sediment all of sampling point in Tunggak River were presented in Table 4.52 and illustrated in Figure 4.92, respectively.

Element	Location 1	Location 2	Location 3
Al	0.783±0.051	1.138±0.173	0.833±0.112
Cr	0.684±0.116	0.842±0.132	0.886 ± 0.075
Mn	0.454±0.116	0.390 ± 0.045	0.499 ± 0.056
Fe	1.000 ± 0.000	1.000 ± 0.000	1.000 ± 0.000
Ni	0.386 ± 0.030	0.658±0.167	0.704 ± 0.335
Cu	0.544 ± 0.096	0.578±0.111	1.051±0.206
Zn	2.587±0.781	2.622±0.326	5.184±0.732
As	11.045±1.598	6.475±2.676	5.278±1.341
Cd	4.070±3.143	20.238±4.098	3.444±1.008
Pb	2.939±0.552	1.669±0.684	2.540±0.929

Table 4.52 Enrichment Factors for stream sediments of study area.

The results showed that all the stream sediments are significantly enriched with As with EF range of 5.278-11.045. All the site sampling sediments with respect to Al, Cr, Mn, Ni, and Cu have enrichment factors of less than 2 and can therefore be classified as deficiency to minimal enrichment. The Enrichment Factor values also indicate that Zn, Cd and Pb, enrichment factor values ranging between 2 until 5, can therefore be classified as moderate enrichment, As enrichment factor values ranging between 5 until 20, can therefore be classified as significant enrichment. Location 1 and 2, appear to be significantly enriched with As. The highest EF value of 11.045±1.598 for As was recorded in location 1, lowest in location 2 and 3 were 6.475±2.676 and 5.278±1.341, respectively. Cadmium appeared to be enrichment in location 1 than location 2 and 3. The EF values of Cd for location 1, 2, and 3 were 4.07±3.143, 20.238±4.098, and 3.444±1.008, respectively. Plumbum has similar value EF in location 1 and 3 were 2.939±0.552 and 2.540±0.929, respectively, and lowest in location 2 was 1.669±0.684. Zn has the similar results in location 1 and 2 were 2.587±0.781 and 2.622±0.326, respectively, highest value EF in location 3 was 5.184±0.732.



Figure 4.92. Enrichment Factor (EF) in sediment in sampling sites of Tunggak River

The Contamination Factor (CF) and Pollution Load Index (PLI) sediment sample all of location in Tunggak River are shown in Table 4.53 and depicted in Figure 4.93 and 4.94

Element	Location 1	Location 2	Location 3
Al	0.119±0.019	2.110±0.006	1.286±0.014
Cr	0.109±0.024	0.308±0.004	0.103±0.013
Mn	0.057±0.005	0.179±0.025	0.058 ± 0.007
Fe	0.128±0.004	3.736±0.009	1.395±0.015
Ni	0.074±0.027	0.246±0.090	0.077±0.011
Cu	0.089 ± 0.022	0.281±0.099	0.107±0.021
Zn	0.504±0.117	1.306±0.206	0.458 ± 0.067
As	1.184±0.327	2.796±1.034	0.708 ± 0.040
Cd	5.392±2.471	16.048±5.661	5.477±3.589
Pb	0.334±0.067	0.814±0.066	0.322±0.039
Pollution			
Load Index			
(PLI)	0.242	1.037	0.371

Table 4.53. Contamination Factor and Pollution Load Index of Sediment

The CFs result shows that all the location had high levels of Cd in their sediment in the order: location 2 (16.048±5.661)> location 3 (5.477±3.589)> location 1 (5.392±2.471). Location 2 sediment recorded the highest CF value of As (2.796±1.034), followed location 1 registered As CF values (1.184±0.327), last location 3 registered As CF values (0.708±0.040). The highest CF value (1.306±0.206) for Zn was found at location 2 sediment samples. The CF values of Zn recorded for in location 1 and 2 sediment samples less than 1.0 were (0.504±0.117) and (0.458±0.067), respectively. Location 2 had the highest CF value for Fe (3.736±0.009), and location 3 followed with (1.395±0.015), and location 1 recorded CFs for Fe (0.128±0.004). Location 2 had the highest recorded Al CF value of (2.110±0.006), followed by location 3 (1.286±0.014), and location 1 (0.119±0.019). Location 1, 2 and 3, recorded CF values less than 1.0 for Cr, Mn, Ni and Cu. Value of Contamination Factor (CF) presented in Figure 4.94.

The sampling points show variations in the PLI values. However, location 3 and location 2 had the PLI values <1.0 (table 4.45). These values are an indication of "unpolluted" within grade 1, while location 3 is indicated "Baseline level of the pollutant present" within grade 2. The overall Pollution Load Indices for the stream sediment sample were found to be in the order: Location 2 (PLI = 1.037) > location 3 (PLI = 0.371) > location 1 (PLI=0.242). A comparative diagram of the PLI values in stream sediment samples is presented by Figure 4.95.

UMP



Figure 4.93. Contamination Factor (CF) in sediment in sampling sites of Tunggak River



Figure 4.94. Comparison Pollution Load Index of sediment sample Tunggak River

The Contamination Factor and PLI of water sample in all of sampling point in Tunggak River as shown in Table 4.54 and showed in Figure 4.95 & 4.96.

Elements	Location 1	Location 2	Location 3
Al	4.011±2.002	11.915±7.949	6.250 ± 2.576
Cr	1.814±0.193	6.381±3.411	1.697 ± 0.287
Mn	0.691±0.253	0.934±0.119	0.048±0.024
Fe	1.331±0.140	2.481±0.634	4.711±2.343
Ni	0.612±0.106	0.791±0.244	0.843±0.204
Cu	1.052±0.271	1.952±0.351	1.642±0.108
Zn	1.911±0.317	1.641 ± 0.201	2.145±0.218
As	14.195±3.502	16.677±8.197	10.377±4.111
Cd	22.794±4.601	2.109±0.341	24.391±8.591
Pb	9.725±1.824	7.611±3.452	16.533±6.051
Pollution Load Index (PLI)	2.017	1.812	1.643

Table 4.54 Contamination Factor (Cf) of streams for the elements Al, Cr, Mn, Fe, Ni, Cu, Zn, As, Cd, and Pb.

The CFs result shows that all the location had high levels of Cd in their water in the order: location 1 (22.794 \pm 4.601)> location 3 (24.391 \pm 8.591)> location 2 (2.109 \pm 0.341). Location 2 water recorded the highest CF value of As (16.677 \pm 8.197), followed location 1 registered As CF values (14.195 \pm 3.502), last location 3 registered As CF values (10.377 \pm 4.111). The highest CF value (16.533 \pm 6.051) for Pb was found at location 3 water samples. The CF values of Pb recorded for in location 1 and 2 water samples were (9.725 \pm 1.824) and (7.611 \pm 3.452), respectively. Location 2 had the highest CF value for Al (11.915 \pm 7.949), and location 3 followed with (6.250 \pm 2.576), and location 1 recorded CFs for Al (4.011 \pm 2.002). Location 3 had the highest recorded Zn CF value of (2.145 \pm 0.218), followed by location 1 (1.911 \pm 0.317), and location 2 (1.641 \pm 0.201). Location 1 had recorded Cu CF value of (1.052 \pm 0.271), followed by location 2 (1.952 \pm 0.351), and location 3 (1.642 \pm 0.108). The highest CF value (6.381 \pm 3.411) for Cr was found at location 2 water samples. The CF values of Cr value of Cr values for Al (1.697 \pm 0.287), respectively. Location 3 and (1.697 \pm 0.287), respectively. Location 3 water recorded the highest CF value of Fe (4.711 \pm 2.343),

followed location 2 registered As CF values (2.481±0.634), last location 1 registered As CF values (1.331±0.140). Location 1, 2 and 3, recorded CF values less than 1.0 for Mn, and Ni. Value of Contamination Factor (CF) presented in Figure 4.95.

The sampling points show variations in the PLI values. However, all the sampling points have the PLI values >1.0 (Table 4.46). These values are an indication of "Baseline level of a pollutant" within grade 2. The overall Pollution Load Indices for the stream water sample were found to be in the order: Location 3 (PLI = 2.643) > location 1 (PLI = 2.017) > location 2 (PLI=1.812). A comparative diagram of the PLI values in stream water samples is presented by Figure 4.96.



Figure 4.95. Contamination factor in water sampling sites of Tunggak River



Figure 4.96. Pollution Load Index water sample of Tunggak River



CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 INTRODUCTION

These chapters conclude the work in this thesis and give some topics for further research study.

5.2 CONCLUSION

This research showed that water in Balok and Tunggak River contain heavy metal such as aluminum, chromium, manganese, ferrum, nickel, copper, zinc, arsenic, cadmium, and plumbum, above the critical limits based on INWQS. From the comparison of accumulated heavy metals in water and sediment, it can be concluded that the heavy metals are highly accumulated in sediments than water, since the sediments has been reported act as the reservoir for all contaminants and dead organic matter descending from the ecosystem above.

The average values recorded for aluminum, ferrum, cadmium in Balok River were above the INWQS thresholds level for all class. However, for manganese, nickel and arsenic values were within the INWQS threshold level for class IV. Meanwhile, zinc and plumbum were within the INWQS threshold level for class II. The average heavy metal concentration accumulated in water Balok River can be presented in the descending order as follows: 212.95 ppm of Fe> 2.31 ppm of Zn> 1.65 ppm of Al> 0.80 ppm of Pb> 0.45 ppm of Cr> 0.19 ppm of Ni> 0.17 ppm of Mn> 0.16 ppm of Cu> 0.14 ppm of As> 0.03 ppm of Cd. While for the average heavy metal concentration accumulated in sediment of Balok River can be presented in the descending order as follows: 9636.94 ppm of Al> 5954.31 ppm of Fe> 22.31 ppm of Mn> 11.61 ppm of Cr> 11.60 ppm of Zn> 11.09 ppm of Pb> 4.89 ppm of Cu> 2.62 ppm of Ni> 2.20 ppm of As> 0.32 ppm of Cd.

In Tunggak River, the average values of chromium, ferrum and cadmium were recorded to be above the INWQS thresholds level for all class. However, the average values of aluminum, manganese, nickel, copper, arsenic, and plumbum were above the INWQS thresholds level for class IV. While the remaining, zinc within the INWQS threshold level for class II. The average values of heavy metal concentration accumulated in water of Tunggak River was as the following order; 6.10 ppm of Fe> 0.86 ppm of Zn> 0.74 ppm of Al> 0.62 ppm of Cr> 0.51 ppm of Pb> 0.48 ppm of Mn> 0.21 ppm of As> 0.14 ppm of Ni> 0.06 ppm of Cu> 0.04 ppm of Cd. However, the average values of heavy metal concentration accumulated in sediment of Tunggak River displayed the following order; 9567.60 ppm of Al> 6174.50 ppm of Fe> 49.54 ppm of Cu> 1.97 ppm of Zn> 9.43 ppm of Cr> 6.19 ppm of Pb> 5.25 ppm of Ni> 4.38 ppm of Cu> 1.97 ppm of As> 0.14 ppm of Cd. In both rivers, it is believed that the present of heavy metal has been proven influenced by human activity, especially from chemical industry, chipboard industry, and domestic disposal waste.

From the correlation elements in water and sediment, it is clearly show that aluminum and ferrum dominated correlation with chromium, copper, zinc, arsenic, cadmium, and plumbum in both rivers with high positive correlation. These criteria thus suggested a common pollution origin for these elements and having similar geochemical behaviors. Based on weak correlation coefficient for element in both rivers poor relationship has been established between water and sediment elements concentrations in Balok River and Tunggak River due to flow rate, water purity and the changing environmental condition.

Based on the statistical analysis of heavy metal by Principal Component Analysis, that sources of pollution are from anthropogenic activities, such as chemical industry, electronic and steel production waste, corrosion of galvanoiz pipe, discharge metal from refinery and corrosion of household plumbing systems. Meanwhile, natural sources of a pollutant are from the erosion of natural deposits, leaching bedrock, and etc.

In this study from an Enrichment Factor analysis, the contaminated sediments of both rivers by cadmium, plumbum, arsenic and zinc level are clearly contributed by the anthropogenic activity such as from chemical industry nearby as well as from the domestic waste. The sediment of Balok River is significantly enriched with cadmium with Enrichment Factor in the range 9.465-52.532. As the Cd Enrichment Factor ranges between 5 until 20, and therefore it can be classified as significant enrichment. For Arsenic, it is appeared that the enrichment in the range of 7.641 - 9.686. As the As Enrichment Factor values ranging between 5 until 20, it is can be classified as significant enrichment. Meanwhile, for plumbum as it is appeared that the Enrichment Factor is in the ranges of 3.276 - 6.688. Thus, as the plumbum Enrichment Factor value ranging between 2 until 5 it is then can be further classified as moderate enrichment. In conclusion, the Enrichment Factor depicted by Cd, As and Pb may indicated that their presences with respect to aluminum, chromium, manganese, nickel, zinc, and copper, in the River may be resulted in from anthropogenic impacts. The Enrichment Factor of less than 2 can therefore be classified as deficiency to minimal enrichment range and would be considered to natural variability.

Meanwhile for Tunggak River, the result shows that its sediments significantly enriched with Enrichment Factor range of 5.18 - 11.045. The As Enrichment Factor ranges between 5 until 20, and therefore can be classified as significant enrichment. For Cadmium, it is appeared that the enrichment in the range of 3.444 - 20.238. As the Cd Enrichment Factor values ranging between 5 until 20, it is can be classified as significant enrichment. Meanwhile, for plumbum as appeared the Enrichment Factor is in the ranges of 1.669 - 2.939. Thus, as the plumbum Enrichment Factor value ranging between 2 until 5 it is then can be further classified as moderate enrichment. The last, for zinc appeared to be enrichment in range 2.587 - 2.622 indicate that zinc Enrichment Factor values ranging between 2 until 5 can therefore be classified as moderate enrichment. In conclusion, the Enrichment Factor depicted by Cd, As, Pb and Zn may indicated that their presences with respect to aluminum, chromium, manganese, nickel, zinc, and copper, in the River may be resulted in from anthropogenic impacts. The Enrichment Factor of less than 2 can therefore be classified as deficiency to minimal enrichment range and would be considered to natural variability.

The Pollution Load Indices (PLI) for the water sample Balok River were found is 3.221 and sediment sample Balok River were 0.848 therefore indication of "Baseline level of pollutant" within grade 2. Meanwhile, the Pollution Load Indices (PLI) for the water sample Tunggak River were found is 2.643 and sediment sample Tunggak River were 0.55 therefore indication of "Baseline level of pollutant" within grade 2. This baseline data is important for decision making processes, designing management involving natural resources, and conservation policies of the Balok River and Tunggak River.

5.3. **RECOMMENDATION**

- Local authority is needed to be more active in river monitoring activities. Always make the study about the effluent standard discharge into the river as a good water management indication. Improvement policy for river preservation river system and make team work, which will be responsible to control the pollution in the river.
- 2. An online monitoring system should be installed by the authority to monitor the pollution discharge by all the industrial waste water.

5.4. FUTURE RESEARCH

- 1. It is recommended that multivariate statistical methods will be integrated in future studies for a particular of pollution risk assessment of atmospheric, soil and water environment in Gebeng area.
- 2. Further investigations should be conducted on the impact assessment of heavy metals in especially those in the industrial area

REFERENCES

- Abbasi, S. A.; Abbasi, N.; Soni, R., 1998. Heavy metal in the environment, 1st. Ed., Mital Publication, New Delhi, India.
- Abraham, G.M. S., & Pareker, R. J. (2008). Assessment of heavy metal enrichment factors and the degree of contamination in marine sediments from Tamaki Estuary, Auckland, New Zealand. *Environmental Monitoring and Assessment*, 136, 227 – 238.
- Abul Kashem,M. D., Singh, B. R., & Kawai, S., 2007.Mobility and distribution of cadmium, nickel and zinc in contaminated soil profiles from Bangladesh. *Nutrient Cycling in Agroecosystems*, Vol. 77, pp: 187–198.
- Ackay, H., Oguz, A., & Karapire, C., 2003. Study of heavy metal pollution and specification in Buyak Menderes and Gediz river sediments. Water Research, Vol. 37, pp: 813-822
- Adamo, P., Arienzo, M., Imperato, M., Naimo, D., Nardo, G., and Stanziones, D., 2005. Distribution and partition of heavy metals in surface and sub-surface sediments of Naples city port. *Chemosphere*, Vol. 61. pp: 800-809.
- Adokokoh, C.K., Obodai, E.A., Essumang, D.K., Serfor-Armah, Y., Nyarco, B.J.B., and Asabere-Ameyaw, A. 2010. Statistical evaluation of environmental contamination, distribution and sources assessment of heavy metals, (Aluminum, Arsenic, Cadmium, and Mercury) in some Lagoons and an estuary along the coastal belt of Ghana. *Arch Environ Contam Toxicol*, doi. 10.1007/s00244-011-9643-5.
- Adomako, D., Nyarko, B. J. B., Dampare, S. B., Serfor-Armah, Y., Osae, S., Fianko, J. R. and Akaho, E. H. K., 2008. Determination of toxic elements in waters and sediments from River Subin in the Ashanti Region of Ghana. *Environ Monit Assess*; Vol. 141, pp: 165–175.
- Adriano, D.C., 2001. (Ed). Trace elements in Terrestrial environments: Biogeochemistry, Bioavailability and Risk of Metals. Springer-Verlag, New York, 2nd edn., 866.
- Aksu, A. E., Yasar, D., & Uslu, O., 1998. Assessment of marine pollution in Izmir Bay: Heavy metal and organic compound concentrations in surficial sediments. *Translations and Journal of Engineering and Environmental Science*, Vol. 22, pp: 387–415.

- Aksoy A, Sahin U & Duman F., 2000. Robinia pseudo-acacia (L.) as a possible biomonitor of heavy metal pollution in Kayseri, Turkish. *Journal of Botany*, Vol. 24, pp: 279–284.
- Al-Khasman, O.A., Shawabkeh, R.A., 2006. Metals distribution in soil around the cement factory in Southern Jordan. *Environmental Pollution*, Vol. 140, (3), pp: 387-394.
- Al-Masri, M. S., Aba, A., Khalil, H., & AL-Hares, Z., 2002. Sedimentation rates and pollution history of a dried lake: ALOteibeh lake. Science of the Total Environment, Vol. 293, pp: 177–189.
- Allan RJ., 1986. The role of particulate matter in the fate of contaminants in aquatic ecosystems. Environment Canada, Inland Waters Directorate, Burlington, Ontario, Canada.
- Allan, I. J., Vrana, B., Greenwood, R., Mills, G. A., Knutsson, J., Holmberg, A., et al., 2006. Strategic monitoring for the European water framework directive. TrAC, *Trends in Analytical Chemistry*, Vol. 25. pp:704–715.
- Alloway, B.J., 1990. Heavy Metals in Soil. Jhon Wiley and Sons, Glasgow, London.
- Alloway, B.J., Ayres, A.K., 1997. Chemical Principles of Environmental Pollution, second ed. Blackie/Chapman and Hall, London/New York, p. 214.
- Alloway, B.l., Thornton, 1., Smart, G.A., Sherlock, *l.C.*, Quinn, MJ., 1988. Metal availability. *The Science of the Total Environment*, Vol. 75. pp: 41-69.
- Anderson, R.A., 1997. Regul. Toxicol. Pharm. Vol. 26, S35.
- Angulo, E., 1999. The Tomlinson Pollution Load index applied to heavy metal, 'Mussel-watch' data: a useful index to assess coastal pollution. Sci Total Environ, Vol. 187 (1), pp: 19-56.
- Ankley, G. T., Lodge, K., Call, D. J., Balcer, M. D., Brooke, L. T., Cook, P. M., et al., 1992. Integrated assessment of contaminated sediments in the lower Fox River and Green Bay Wisconsin. *Ecotoxicology and Environmental Safety*, Vol. 23(1), pp: 46–63.
- Anon. b., 1996. South African water quality guidelines. 2nd Edition, Domestic Use 1, Department of Water Affairs and Forestry, South African.
- Aurada, K. D., 1983, 'Physiographic and Anthropogenic Controls of Global and Regional Ionic Runoff', in: B. W. Webb (ed.), Proceedings of Symposium on Dissolved Loads of Rivers and Surface Water Quantity/Quality Relationship, Hamburg, IAHS Publ. No. 141, 31–39.

- ATSDR, 2005. "Toxicological Profile for Lead, Public Health Statement," available at http://www.atsdr.cdc.gov/ toxprofiles/phs2.html (last visited July, 25, 2011).
- ATSDR, 2007. "Toxicological Profile for Arsenic, Public Health Statement," available at http://www.atsdr.cdc.gov/ toxprofiles/phs2.html (last visited Nov. 19, 2010).
- Aydin, O. 2004. Investigations for estimating and improving the water quality at Karasu Valley in Nigde. Master's thesis, Nigde University, p. 75 (in Turkish with English abstract).
- Aziz, H.A., Adlan, M.N and Ariffin, K.S., 2008. Heavy metals (Cd, Pb, Zn, Ni, Cu and Cr(III)) removal from water in Malaysia: Post treatment by high quality limestone. *Biores. Technol.* Vol.99, pp: 1578-1583
- Bai, J., Xiao, R., Cui, B., Zhang, K., Wang, Q., Liu, X., Gao, H., and Huang, L., 2011. Assessment of heavy metal pollution in wetland soils from the young and old reclaimed regions in the Pearl River Estuary, South China. J. Environmental Pollution, Vol. 159. pp: 817-824.
- Baptista Neto, J. A., Smith, B. J., & McAllister, J. J., 2000. Metal concentrations in surface sediments in a nearshore environment, Jurujuba Sound, Southeast Brazil. *Journal Environmental Pollution*, Vol. 109, pp: 1–9.
- Barroso, M.R.R., Benhamou, Y., EI Moumni., El Hatimi, & Morales, J.L.G., 2009. Evaluation of metal contamination in sediments from north of Morocco: geochemical and statistical approaches. *Environ Monit Assess*, Vol. 159. pp: 169-181.
- Barroso MRR, Morales JLG, Oviedo MDC, and Alonso JMQ., 2010. An assessments of heavy metal contamination surface sediment using statistical analysis. J. Environ Monit Assess. Vol. 163, pp:489-501.
- Batty, L.C., Younger, P.L., 2007. The effect of pH on plant litter decomposition and metal cycling in wetland mesocosms supplies with mine drainage. *Journal Chemosphere*, Vol. 66 (1), pp: 158-164.
- Begum, A., HariKrishna, S., Khan, I., 2009. Analysis of Heavy metals in Water, Sediments and Fish samples of Madivala Lakes of Bangalore, Karnataka. Int. J. of ChemTech Res. Vol. 1(2), pp: 245-249.
- Bengtsson, G., Nordstorm, S., Rundgren, S., 1981. Population density and tissue metal concentration of lumbricids in forest soils near a brass mill. *Environmental Pollution* Vol. 30, pp: 87-108
- Berg H, Kiibus M, Kautsky N., 1995. Heavy metals in tropical Lake Kariba, Zimbabwe. *J. Wat Air Soil Pollut*. Vol. 82. pp: 1-6.

- Bergasmaschi, L., Rizzio, E., Valuvia, M. G., Verza, G., Profumo, A., & Gallorini, M., 2002. Determination of trace elements and evaluation of their enrichment factors in Himalayan lichens. *Journal Environmental Pollution*, Vol. 120 (1), pp: 137 – 144. doi: 10.1016/S0269-7491(02)00138-0.
- Berner, E.A. and Berner, R.A., 1987 *The Global Water Cycle, Geochemistry and Environment.* Prentice Hall, Englewood Cliffs, Mich., 397 pp
- Bettinetti, R., Giarei, C., & Provini, A., 2003. A chemical analysis and sediment toxicity bioassays to assess the contamination of the River Lambro (Northern Italy). *Archives of Environmental Contamination and Toxicology*, Vol. 45, pp: 72–80. doi:10.1007/s00244-002-0126-6.
- Bhuiyan, M. A. H., Suruvi, N. I., Dampare, S. B., Islam, M A., Quraishi, S. B., Ganyaglo, S., et al., 2010. Investigation of the possible sources of heavy metals contamination in lagoon and canal water in the tannery industrial area in Dhaka, Bangladesh. *Journal Environmental Monitoring and Assessment*. doi:10.1007/s10661-010-1557-6.
- Binelli, A., Sarkar, S.K., Chatterjee, M., Riva, C., Parolini, M., Bhattacharya, B. D., et al., 2008. A comparison of sediment quality guidelines for toxicity assessments in the Sunderban wetland (Bay of Bengal, India). *Chemosphere*, Vol.73, pp: 1129-1137.
- Birch, G., McCready, S., Taylor, S., Spyrakis, G., Long, E., 2008, Contaminant chemistry and toxicity of sediments in Sydney Harbour Australia: spatial extent and chemistry-toxicity relationships, *Marine Ecology Progress Series*, Vol. 363, pp: 71-87.
- Boonyatumanond, R., Wattayakorn, G., Amano, A., Inouchi, Y., Takada, H., 2007.Reconstruction of pollution history of organic contaminants in the upper Gulf of Thailand by using sediment cores: first report from Tropical Asia Core (TACO) project. *Marine Pollution Bulletin*, Vol. 54, pp: 554-565.
- Boruvka, L., Vecek, O., Jenlika., 2005. Principal component analysis as a tool to indicates the origin of potentially toxic elements in soil. *Geoderma*, Vol. 128. pp: 289-300.
- Botalova, O., and Schwarzbauer, J., 2011. Geochemical characterization of organic pollutants in effluents discharged from various industrial sources to riverine systems. *Water Air Soil Pollut*. DOI 10.1007/s11270-011-0771-3.
- Boxall ABA, Maltby L., 1995. The characterization and toxicity of sediment contaminated with road runoff. *Water Res*, Vol. 29, pp: 2043-2050.
- Boyle, R.W., 1981. Geochemistry of nickel. In: Effects of nickel in the Canadian environment, Ottawa, National Research Council of Canada, pp. 31-44 (Publication No. NRCC 18568).
- Brown, J. N., 2002. Partitioning of chemical contaminants in urban storm water. Dunedin, New Zealand: University of Otago.

- Brown JN, Peake BM (2006): Sources of heavy metals and polycyclic aromatic hydrocarbons in urban stormwater runoff. Sci Tot Environ 359: 145-155.
- Bruins, M. R.; Kapil, S.; Oehme, F. W., 2000. Microbial resistance to metals in the environment. Ecotox. Environ. Safe. Vol. 45, pp: 198-207.
- Bu, H., Tan, X., Li, S., and Zhang, Q., 2010. Water quality assessment of the Jinshui River (China) using multivariate statistical techniques. *Journal Environ Earth Sci*, Vol. 60, pp: 1631-1639. doi:10.1007/s12665-009-0297-9.
- Buccolieri A., Buccolieri G., Cardellicchio N., Atti A.D., Leo., A.D., and Antonella M., 2006. Heavy metals in marine sediments of Taranto Gulf (Lonian Sea, Southern Italy). *Marine Chemistry*. Vol. 99, pp: 227-235.
- Burton E, Phillips I, Hawker D., 2004. Trace metals and nutrients in bottom sediments of the southport Broadwater, Australia. *Mar Pollut Bull*. Vol. 48. pp:378–384.
- Burt, R., Wilson, M. A., Keck, T. J., Dougherty, B. D., Strom, D. E., & Lindahld, J. A., 2003. Trace element speciation in selected smelter-contaminated soils in Anaconda and Deer Lodge Valley, Montana, USA. Advances in Environmental Research, Vol. 8, pp: 51–67.
- Butt, E.M., Nusbaum, R.E., Gilmour, T.C., Mariano, S.X., and Didio, S.L., 1964. Trace metal in levels in human serum and blood. *Arch. Environ. Health*, Vol. 8, pp: 52-57.
- B'Hymer, Clayton, Judith A. Brisbin, Karen L. Sutton, and Joseph A. Caruso., 2000."New approaches for elemental speciation using plasma mass spectrometry." American Laboratory. Vol. 32(3), pp: 17-32.
- Cabrera, F., Clemente, L, Barrientos, D.E., Lopez, R., and Murillo, J.M. 1999. Heavy metal pollution of soil affected by Guandiamar toxic flood. Sci. Total Environ. Vol. 242, pp: 117 129.
- Caccia, V., Millero, F.,&Palanques, A., 2003. The distribution of trace metals in Florida Bay sediments. *Marine Pollution Bulletin*. Vol. 46. pp:1420–1433.
- Carlon, C., Critto, A., Marcomini, A., Nathanail, P., 2001. Risk based characterization of contaminated industrial site using multivariate and geostatistical tools, *Journal Environmental Pollution*, Vol. 111, pp: 417-427.
- Cevik F, Goksu M, Derici O, Findik O., 2009. An assessment of metal in surface sediments of Seyhan dam by using enrichment factor, geoaccumulation index and statistical analyses. *Environmental Monitoring and Assessment*. Vol. 148. pp: 291-305.

- Cevik, F., Goksu, M. Z., Derici, O. B., & Findik, O. (2009). An assessment of metal pollution in surface sediments of Seyhan dam and by using enrichment factors, geoaccumulation index and statistical analyses. *Journal Environmental Monitoring and Assessment*, Vol. 152 (1 – 4), pp: 309 – 317.
- Chan KM., 1995a. Concentrations of Copper, Zinc, Cadmium, and Lead in Rabbit fish *(Siganus oramin)* collected in Victoria Harbour, Hong Kong. *Mar Pollut Bull*. Vol. 31. pp: 277-280.
- Chan KM., 1995b. Methallothionein: Potential Biomarker for monitoring Heavy metal pollution in fish around Hong Kong. *Mar Pollut Bull*. Vol. 31. pp: 411-415.
- Chapman PM, McDonald BG, Lawrence GS. 2002. Weight-of-evidence issues andframeworks for sediment quality (and other) assessments. *Hum Ecol Risk Assess.* Vol. 8, pp: 1489-1515.
- Cheevaporn V, Jacinto GS, San Diego-McGlone S., 1995. Heavy metal fluxes in Bang Pakong River Estuary, Thailand: sedimentary vs diffusive fluxes. *Mar Pollut Bull*. Vol. 31. pp: 290-294.
- Chen, W., Tan, S.K., and Tay, J.H., 1996. Distribution, fractional composition and release of sediment-bound heavy metals in tropical reservoir. *Water Air Soil Pollut*. Vol. 92. pp: 273-287.
- Chen, K., Jiao, J.J., Huang, R., 2007. Multivariate statistical evaluation of trace elements in groundwater in coastal area in Shenzhen, China. *Environ Pollut*, Vol. 147, pp: 771-780.
- Cheung, K.C., Poon, B.H.T., Lan, C.Y., and Wong, M.H., 2003. Assessment of metal and nutrient concentrations in river water and sediment collected from the cities in the Pearl River Delta, South China. *Chemosphere*. Vol. 52. pp: 1431-1440.
- Christophoridis, C., Dedepsidis, D., & Fytianos, K., 2009. Occurrences and distribution of selected heavy metals in the surface sediments of Thermaikos Gulf, N. Greece. Assessment using pollution indicators. *Journal of Hazardous Material*, Vol. 115, pp: 1082 – 1091.

Clark, R.B., 1997. Marine Pollution, 4th ed. Clarendon Press, Oxford

- Clark R.B., 2001, *Marine Pollution*. Fifth edition. Pages 1-231. Oxford University Press Inc., New York. 2001.
- Cundy, A. B., Croudace, I. W., Cearreta, A., & Irabien, M. J., 2003. Reconstructing historical trends in metal input in heavily-disturbed, contaminated estuaries: studies from Bilbao, Southampton Water and Sicily. *Applied Geochemistry*. Vol. 18. pp: 311–325.
- Connell, D.W., Miller, J.G., 1984. Chemistry and Ecotoxology of Pollution, Jhon Wiley&Sons, New York.

- Conrad, C. F., & Chisholm-Brause, C. J. (2004). Spatial survey of trace metal contaminants in the sediments of the Elizabeth River, Virginia. *Journal Marine Pollution Bulletin*, Vol. 49, pp: 319 324.
- Coker, W. B., Kettles, I. M., & Shilts, W. W., 1995. Comparison of mercury concentrations in modern lake sediments and glacial drift in the Canadian Shield in the region of Ottawa/Kingston to Georgian Bay, Ontaria, Canada. *Water, Air* and Soil Pollution, Vol. 80, pp: 1025–1029.
- Daskalakas, K.D. & O'Connor, T.P., 1995. Normalization and elemental sediment contamination in the Coastal United States. *Environmental Science and Technology*.Vol. 29. pp: 470-477.
- Daskalakis, K. D. and O'Connor, T. P.: 1995, 'Distribution of chemical concentrations in US coastal and estuarine sediment', *Mar. Environ. Res.* Vol. 40, pp: 389–398.
- Dassenakis, M., Scoullus, M., Foufa, E., Kraskopoulou, E., Pavlidou, A., & Kloukiniotou, M., 1998. Effects of multiple sources pollution on a small Mediterranean river. *Appl. Geochem.*, Vol. 13 (2). pp: 197-211.
- Dahlberg, E. C. 1968. Application of selective simulation and sampling technique to the interpretation of stream sediments copper anomalies near south mountain, PA', *Econ. Geol.* Vol 63. pp: 409-417.
- Dickinson, W. W., Dunbar, H. B., & Mcleod, H., 1996. Heavy metal history from cores in Wellington Harbour, New Zealand. *Environmental Geology*, Vol. 27, pp: 59 – 69.
- De Bartolomeo, A., Poletti, L., Sanchini, G., Sebastiani, B., & Morozzi, G., 2004. Relationship among parameters of lake polluted sediments evaluated by multivariate statistical analysis. *Chemosphere*, Vol. 55, pp: 1323–1329.
- Demirak, A., Yilmaz, F., Tuna, L., Ozdemir, N., 2006. Heavy metals in water, sediment and tissues of *Leuciscus cephalus* from a stream in southwestern Turkey. *Chemosphere*, Vol. 63 (9), pp: 1451-1458.
- Department of Environment, 'The monitoring of the environment in the United Kingdom', Report by Central Unit on Environmental Pollution, HMSO, London, 1974. Book "Understanding Our Environment" An introduction to Environmental Chemistry and Pollution. Third Edition. Edited by R.M. Harisson. Published by The Royal Society of Chemistry, Thomas Graham House, Science Park, Milton Road, Cambridge CB4 0WF, UK.
- Di Leonardo, R., Tranchida, G., Bellanca, A., Neri, R., Angelone, M., & Mazzola, S., 2006. Mercury levels in sediments of central Mediterranean Sea: A 150+ year record from box-cores recovered in the Strait of Sicily. *Chemosphere*, Vol. 65, pp: 2366-2376.

- Di Toro, D. M., Zarba, C. S., Hansen, D. J., Berry, W. J., Swartz, R. C., Cowan, C. E., et al., 1991. Technical basis for establishing sediment quality criteria for nonionic organic chemicals by using equilibrium partitioning. *Environmental Toxicology Chemistry*, Vol. 10, pp:1541–1583.
- Duffus, J., 2002. "Heavy metals" a meaningless term? (IUPAC Technical Report). Pure and Applied Chemistry; Vol. 74, pp: 793-807.
- El Diwani, G.; El Rafie, Sh., 2008. Modification of thermal and oxidative properties of biodiesel produced from vegetable oils. *Int. J. Environ. Sci. Tech.*, Vol. 5 (3). pp: 391-400.
- El Nemr, A., Khaled, A., & El Sikaily, A., 2006. Distribution and statistical analysis of leachable and total heavy metals in the sediments of the Suez Gulf. *Environmental Monitoring and Assessment*, Vol. 118, pp: 89–112.
- Elinder CG., 1992. Cadmium as an environmental hazard. *IARC Sci Pu*, Vol. 1118, pp: 123-132.
- Elinder CG. 1985a. Cadmium: Uses, occurrence and intake. In: Friberg L, Elinder CG, Kjellstrom T, et al., eds. Cadmium and health: A toxicological and epidemiological appraisal. Vol. I. Exposure, dose, and metabolism. Effects and response. Boca Raton, FL: CRC Press, 23-64.
- Esen, E., Kucuksezgin, F., & Uluturhan, E., 2010. Assessment of trace metal pollution in surface sediments of Nemrut Bay, Aegean Sea. *Journal Environmental Monitoring and Assessment*, Vol. 160, pp: 257 – 266.
- EPA. 1981a. Health assessment document for cadmium. Research Triangle Park, NC: U.S. Environmental Protection Agency, Environmental Criteria and Assessment Office. EPA-600/8-81-023.
- EPA. 1985a. Cadmium contamination of the environment: An assessment of nationwide risk.
 Washington, DC: U.S. Environmental Protection Agency, Office of Water Regulations and Standards. EPA-440/4-85-023.
- EPA. 1988d. Drinking water regulations; maximum contaminant level goals and national primary drinking water regulations for lead and copper. U.S. Environmental Protection Agency. Fed Regist, Vol. 53(160), pp: 31516-31578.
- EPA. 1985d. U. S. Environmental Protection Agency. National emission standards for hazardous air pollutants: Applicability. Code of Federal Regulations. 40 CFR 61-01.

- EPA,. 2007, "Arsenic in Drinking Water," available at http://www.epa.gov/safewater/arsenic/basicinformation.html (last visited Nov. 19, 2010).
- EPA., 2007, "Arsenic in Drinking Water," available at http://www.epa.gov/safewater/arsenic/basicinformation. html (last visited Nov. 19, 2010);
- Evanko, C.R. & Dzombak, D.A., 1997. Remediation of Metals-Contaminated Soils and Groundwater. *Technology Evaluation Report*, Carnegie Mellon University, Pittsburgh, PA.
- Fernandez D.G., Perez M.C.G., Sanz, E.N., and Marquez D.S., 2011. Source and Fate of Heavy Metals in Marine Sediments from a Semi-Enclosed Deep Embayment Subjected to Severe Anthropogenic Activities. *Water Air Soil Pollut*. Vol 221. pp: 191–202. doi 10.1007/s11270-011-0782-0.
- Fianko, J.R., Osae, S., Adomako, D., Adotey, D.K., Armah, Y.S., 2007. Assessment of heavy metal pollution of the Iture Estuary in the Central Region of Ghana. *Journal Environ Monit Assess*, Vol. 131, pp: 467–473. DOI 10.1007/s10661-006-9492-2.
- Focazio, M. J., Kolpin, D. W., Barnes, K. K., Furlong, E. T., Meyer, M. T., Zaugg, S. D., et al., 2008. A national reconnaissance for pharmaceuticals and other organic wastewater contaminants in the United States—II untreated drinking water sources. The Science of the Total Environment, Vol. 402, pp: 201–216.
- Forstner, U., & Muller, G., 1973. Heavy metal accumulation in river bed sediments: A response to environmental pollution. *Geoforum*. Vol, 14. pp: 53-61.
- Forster, C.F. and Wase, D.A.J., 1997. Biosorption of heavy metals: An introduction. In: Biosorbents for Metals Ions, [Chapter 1.] Wase, D.A.J. and Forster, C. (ed), Taylor&Francis, London.
- Frickel, S., Elliott, J.R., 2008. Tracking industrial land use conversions: a new approach for studying relict waste and urban development. Organization & Environment. Vol. 21 (2), pp: 128-147.
- Frignani M., Belluci L.G., Langone L., Muntaun H., 1997 Metal fluxes to the sediments of the northen Venice Lagoon. *Marine Chemistry*, Vol. 58, pp: 275-292.
- Frignani, M., & Belluci, L.R., 2004. Heavy Metals in Marine Coastal Sediments: Assessing sources, fluxes, History and Trend. Annali di Chimca, Vol. 94, pp: 479-486.
- Fukue M., Nakamura T., Kato Y., Yamasaki S., 1999. Degree of pollution for marine sediment. *Engineering geology*. Vol. 53, pp: 131-137.

- Garbarino, J. R., Antweiler, R. C., Brinton, T. I., Roth, D. A., & Taylor, H. E., 1995. Concentration and transport data for selected dissolved inorganic constituents and dissolved 174 Environ Monit Assess., 2008. Vol. 141., pp:165–175 organic carbon in water collected from the Mississippi River and some of its tributaries, July 1991–May 1992.
- Garbisu, C., & Alkorta, I., 2001. Phytoextraction: A cost-effective plant-based technology for the removal of metals from the environment. *Bioresource Technology*, Vol. 77, pp: 229–236.
- Garrels, R.M., Mackenzi, F.T. & Hunt, C. 1975. in: C.A. Williams (ed.), *Chemical cycles and the global environment-assessing human influences*, Kaufman Co., 206 pp.
- Georgopoulos AR, Yonone-Lioy MJ, Opiekun RE, et al., 2001. Environmental copper: Its dynamics and human exposure issues. *J Toxicol Environ Health Part B Crit Rev*, Vol. 4(4), pp: 341-394.
- Ghrefat, H., & Yusuf, N., 2006. Assessing Mn, Fe, Cu, Zn and Cd pollution in bottom sediments of Wadi Al-Arab Dam, Jordan. *Chemosphere*, Vol. 65, pp: 2114– 2121. doi:10.1016/j.chemosphere.2006.06.043.
- Gibbs, R. J., 1972.Water chemistry of the Amazon River. *Geochimica et Cosmochimica Acta*, Vol. 36, pp. 1061–1066. doi:10.1016/0016-7037(72)90021-X.
- Go'mez-Ariza JL, Gira'Idez I, Sa'nchez-Rodas D, Morales E., 1999. Metal read sorption and redistribution during the analytical fractionation of trace elements in oxic estuarine sediments. *Anal Chim Acta*, Vol. 399, pp: 295–307. doi:10.1016/S0003-2670(99) 00460-2.
- Gonzalez-Macias C, Schifter I, Liuch-Cota DB, Mendez-Rodriguez L, Hernandez-Vazquez S 2006. Distribution, enrichment and accumulation of heavy metals in coastal sediments of Salina Cruz Bay, Mexico. *Environ Monit Assess*, Vol. 118. pp.211–230.
- Handvosky, H., 1926. The acute and chronic heavy metal poisoning II announcement-Impact of bivalent tin. Naunyn-Schmiedebergs Arch. Exp. Pathol. Pharmakol., Vol. 114, pp: 39-46.
- Han, Y., Du, P., Cao, J., Posmentier, E.S., 2006. Multivariate analysis of heavy metal contamination in urban dusts of Xi'an, Central China. Science of the Total Environment. Vol. 355. pp: 176-186.
- Hang, X., Wang, H., Zhou, J., Du, C., and Chen, X., 2009. Characteristic and accumulation of heavy metals in sediments originated from an electroplating plant. *Journal of hazardous Material*, Vol. 163. pp: 922-930.
- Harrison BJ. 1998., Table 1. Copper concentrations in the environment. In: Copper information sourcebook- 1998- the world's scientific literature on copper in the environment and health, 21-62.

- Harrison FL, Bishop DJ., 1984. A review of the impact of copper released into freshwater environments. U.S. Nuclear Regulatory Commission. Livermore, CA: Lawrence Livermore National Laboratory. NUREG/CR-3478.
- Hauri J. F., Jr., 2001. Measurement and manipulating of copper specification and toxicity in urban Runoff, Acid Mine Drainage, and contaminated discharged groundwater. Ph.D. Disertation. University of California, Berkeley.
- Hecker, L.H., Allen, H.E., Dinman, B.D., and Neel, J.V., 1974. Heavy metal levels in acculturated and unacculturated populations. Arch. Environ. Health, Vol. 29, pp: 181-185.
- Hem, J.D., 1989 Study and Interpretation of the Chemical Characteristics of Natural Water. U.S. Geological Survey Water Supply Paper No. 2254, 263 pp.
- Hoekman, T., 2008. Heavy metal toxicology. [www.ucs.mun.ca/~thoekman], (accessed 2010 November 13).
- Hernandez, L., Probst, A., Probst, J. L., & Ulrich, E., 2003. Heavy metal distribution in some French forest soils: Evidence for atmospheric contamination. *The Science* of the Total Environment., Vol. 312, pp: 195–219. doi:10.1016/S0048-9697(03)00223-7.
- Hewitt, J. E., Anderson, M. J., Hickey, C.W., Kelly, S., & Thrush, S. F., 2009. Enhancing the ecological significance of sediment contamination guidelines through integration with community analysis. *Environmental Science & Technology*, Vol. 43, pp: 2118–2123.
- Hollert, H., Keiter, S., Konig, N., Rudolf, M., Ulrich, M., & Braunbeck, T., 2003. A new sediment contact assay to assess particulate-bound pollutants using Zebrafish (*Danio rerio*) embryos. *Journal of Soils and Sediments*, Vol. 3, pp: 197–207. doi:10.1065/jss2003.09.085.
- Hopke, P.K., 1985. 'Receptor Modelling in Environmental Chemistry', Jhon Wiley & Sons, New York. Book "Understanding Our Environment" An introduction to Environmental Chemistry and Pollution. Third Edition. Edited by R.M. Harisson. Published by The Royal Society of Chemistry, Thomas Graham House, Science Park, Milton Road, Cambridge CB4 0WF, UK.
- Hopenhayn C., 2006. Arsenic in drinking water: Impact on human health. *Elements*, Vol. 2, pp: 103–107.
- Hornung, H., Karm, M. D., & Cohen, Y., 1989. Trace metal distribution on sediments and benthic fauna of Haifa Bay, Israel. *Estuarine, Coastal and Shelf Science,* Vol. 29, pp: 43 – 56.

Housecroft CE, Sharpe AG. 2008. Inorganic Chemistry. Prentice Hall, Harlow.

- Howari, F.M., 2005. Distribution of Heavy Metal Concentrations in Surface Sediments in Dubai Creeks, United Arab Emirates. *Annali di Chimica*, Vol. 95. Issue 9-10.page n/a. DOI: 10.1002/adic.200590085.
- Hsu, M.J., Selvaraj, K., Agoramoorthy, G., 2006. Taiwan's industrial heavy metal pollution threatens terrestrial biota. *Environmental Pollution*, Vol. 143, pp: 327-334
- Idrees, F. A., 2009. Assessment of trace metal distribution and contamination in surface soils of Amman. Jordan. J. Chem., Vol. 4 (1). pp: 77-87.
- Ip CCM, Li XD, Zhang G, Wai OWH, Li YS., 2007. Trace metal distribution in sediments of the Pearl River Estuary and the surrounding coastal areas, South China. *Env Poll* Vol. 147. pp: 311–323.
- Ives, A.R., Cardinale, B., 2004. Food-Web Interaction Govern The resistance of Communities after Non-Random Extinction. Nature, Vol. 429, pp: 174-177.
- IARC., 1993. Cadmium and certain cadmium compounds. In: IARC monographs on the evaluation of the carcinogenic risk of chemicals to humans. Beryllium, cadmium, mercury and exposures in the glass manufacturing industry. IARC monographs, Vol. 58. Lyon, France: World Health Organization. International Agency for Research on Cancer, 119-146, 210-236.
- IJC., 1989. Report on Great Lakes water quality. Presented at Hamilton, Ontario, October 1989. Windsor, Ontario: international Joint Commission, Great Lakes Water Quality Board.
- Izquirdo, C., Usero, J., & Gracia, I., 1997. Speciation of heavy metals in sediments from salt marches on the southern Atlantic coast of Spain. *Marine Pollution Bulletin*, Vol. 34(2), pp: 123–128.
- Jain, C.K., 2004. Water Res. Vol. 38. pp: 569.
- Jain, C.K., Singhal, D.C., & Sharma, U.K., 2005. Metal pollution assessment of sediment and water in the river Hindon, India. *Environmental Monitoring and Assessment*. Vol. 105. pp: 193-207.
- Jain, C.K. & Sharma, M.K., 2006. Heavy metal transport in the Hindon river basin, India. *Environ Monit Assess*. Vol. 112. pp: 255-270.
- Jarvis, K. E.; A. L. Gray; and R. S. Houk., 1992. Handbook of Inductively Coupled Plasma Mass Spectrometry. Chapman and Hall: New York.
- Jha, S.K., Chavan, S.B., Pandit, G.G., Sadasivan, S., 2003. Geochronology of Pb and Hg pollution in a coastal marine environment using fallout ¹³⁷Cs. *Journal of Environmental Radioactivity*, Vol. 69, pp: 145-157.

- Johnson, F. M., 1998. The genetic effects of environmental lead., *Mutat. Res.*, Vol. 410., 123-140.
- Kazi, T. G., Arain,M. B., Jamali, M. K., Jalbani, N., Afridi, H. I., Sarfraz, R. A., et al., 2009. Assessment of water quality of polluted lake using multivariate statistical techniques: A case study. *Ecotoxicology and Environmental Safety*, Vol. 72, pp: 301–309.
- Kamala-Kannan S., Batvari B.P.D., Lee K.J., Kannan N., Krishnamoorthy R., Shanthi K., Jayaprakash M., 2007. Assessment of heavy metals (Cd, Cr and Pb) in seaweed (Ulva lactuca) in the Publicat Lake, South East India. Chemosphere, Vol. 71, pp: 1233–1240.
- Kar D, Sur P, Saha T, Kole RK., 2008. Assessment of heavy metal pollution in surface water. *Int. J. Environ. Sci. Tech.*, Vol. 5 (1). pp: 119-124.
- Karageorgis, A.P., Katsanevakis, S., & Kaberi, H., 2009. Use of Enrichment Factors for the Assessment of Heavy Metal Contamination in the Sediments of Koumoundourou Lake, Greece. Water Air Soil Pollut. Vol. 204. pp: 243-258. doi: 10.1007/s11270-009-0041-9.
- Kay AL, Jones RG, Reynard NS., 2006.RCM rainfall for UK flood frequency estimation. II. Climate change results. *J Hydrol*, Vol. 318, pp: 163-172
- Kennish, M.J., 1992. Ecology of Estuaries: Anthropogenic Effects. CRC Press, Inc., Boca Raton, FL, 494 pp.
- Keskin, S. 2010. Distribution and accumulation of heavy metals in the sediments of Akkaya Dam, Nigde, Turkey. *Environ Monit Assess.* doi: 10.1007/s10661-011-1979-9.
- Khan A.G., T.M Kuek, CS Chaudhry, and WJ Hayes., 2000. Role of plants, mycorrhizae and phytochelators in heavy metal contaminated land remediation. *Chemosphere*. Vol. 41, pp: 197-207.
- Kim, M., Kennicutt II, M.C., Qian, Y., 2006. Molecular and stable carbon isotopic characteristics of PAH contaminants at MvMurdo Station, Antartica. *Journal Marine ollution Bulletin*, Vol. 52, pp: 1585-1590.
- King M, Ramachandran V., 1995. Lead. In: Kirk-Othmer encyclopedia of chemical technology. 4th edition. New York, NY: John Wiley & Sons, 69-113.
- Klavins, M., Briede, A., Rodinov, V., Kokorite, I., Parele, E., & Klavina, I., 2000. Heavy metals in river of Lativa. *Science of the Total Environment*. Vol. 262. pp: 175–183.

- Kucuksezgin, F., Kontas, A., Altay, O., Uluturhan, E., & Darilmaz, E., 2006. Assessment of marine pollution in Izmir Bay. Nutrient, heavy metal ant total hydrocarbon concentrations. *Environment International*, Vol.32, pp:41–51. doi:10.1016/j.envint.2005.04.007.
- Kummrow, F., Silva, F. F., Kuno, R., Souza, A. L., & Oliveira, P. V., 2008. Biomonitoring method for the simultaneous determination of cadmium and lead in whole blood by electrothermal atomic absorption spectrometry for assessment of environmental exposure. *Talanta*, Vol. 75(1), pp: 246–252.
- Kuppusamy, M.R., Grirdhar, V. V., 2006. Factor analysis of water quality characteristics including trace metal specification in the coastal environmental systems of Chennai Ennore. *Environment International*, Vol. 32, pp: 174-179.
- Korfali, S.I., and Jurdi, M.S., 2011. Specification of metals in bed sediments and water of Qaraaoun Reservoir, Lebanon. *Journal Environ Monit Assess (2011)* 178:563–579. DOI 10.1007/s10661-010-1713-z.
- K.P. Singh, D. Mohan, V.K. Singh, A. Malik., 2005. Studies on distribution and fractionation of heavy metals in Gomti river sediments a tributary of the Ganges, India, *J. Hydrol*. Vol. 312, pp: 14-17.
- Lamb, R. A., 1964. Suggested measure of toxicity due to metals in industrial effluents, sewage and river water. *Air Water Pollutant.*, Vol. 8, pp: 243-249.
- Larison, J.R., Likens, E., Fitzpatrick, J.W., Crock, J.G., 2000. Cadmium Toxicity Among Wildlife in The Colorado Rocky Mountains. Nature, Vol. 406, pp: 181-183.
- Lasheen, M. R. and Ammar, N.S., 2009. Specification of some heavy metals in River Nile sediments, Cairo, Egypt. *Environmentalist*, Vol. 29, pp: 8–16. DOI 10.1007/s10669-008-9175-3.
- Ledin, M., 2000. Accumulation of metals by microorganisms-processes and importance for soil systems. *Earth Sci. Rev.*, Vol. 51, pp: 1-31.
- Lee, C.S.L., Li, X.D., Shi, W.Z., Cheung, S.C., Thornton, J., 2006, Metal contamination in urban, suburban, and country park soils of Hongkong: a study based on GIS and multivariate statistics. *The science of the Total Environment*, Vol. 356 (1-3), pp: 45-61.
- Leivouri, M., 1998. Heavy metal contamination in surface sediments in the Gulf of Finland and comparison with the Gulf of Bothnia. *Chemosphere*, Vol. 36, pp: 723–733.
- Libralato, G., Losso, C., Novelli, A.A., Citron, M., Salla, A.D., Zanotto, E., Cepak, F., Ghirardini, A.A., 2008. Ecotoxological evaluation of industrial port of Venice (Italy) sediment samples after a decontamination treatment, *Journal of Environmental Pollution*, Vol. 156, pp: 644-650.

- Lim PE, Lee CK, Din Z., 1995. Accumulation of heavy metals by cultured oysters from Merbok Estuary, Malaysia. *Mar Pollut Bull*. Vol. 31. pp: 420-423.
- Lin, C.Y., He, M.C., Zhou, Y.X., Guo, W., Yang, Z.F., 2008. Distribution and Contamination Assessmets of Heavy Metals in Sediments of the Second Songhua River, China. *Environ. Monit. Assess.* Vol. 137 (1), pp: 329-342.
- Linnik, P. M.; Zubenko, I. B., 2000. Role of bottom sediments in the secondary pollution of aquatic environments by heavy metal compounds, lakes and reservoirs. *Res. Manage.*, Vol. 5 (1), pp: 11 21.
- Liu B, Hu K, Jiang Z, Yang J, Luo X and Liu A., 2011. Distribution and enrichment of heavy metals in a sediment core from the Pearl River Estuary. *Journal Environ Earth Sci.* Vol. 62, pp: 265-275. doi. 10.1007/s12665-010-0520-8.
- Li, X.D., Lee, S.L., Wong, S.C., Shi, W.Z., and Thorton, I., 2004. The study of metal contamination in urban soils of Hong Kong using a GIS-based approach. *Environmental Pollution*, Vol. 43 (14). pp: 113-124.
- Long, E.R., Macdonald, D.D., Smith, S.L., and Calder, F.D., 1995. Incidence of adverse biological effects within ranges of chemical concentrations in marine and estuarine sediments. *Environ. Manage.*, Vol. 19., pp: 81-97.
- Loska, K., Wiehula, D., 2003. Application of principal component analysis for the estimation of sources heavy metal contamination in surface sediments from Rybnik Reservoir. *Journal Chemosphere*, Vol. 51, pp: 723-733.
- Lottermoser, B.G. 2nd 2007. Mine Wastes: Characterization, Treatment and Environmental Impacts. Edition. Springer-Verlag. Berlin/Heidelberg.
- Luoma, S. N., & Bryan, G. W., 1981. A statistical assessment of the form of trace metals in oxidized estuarine sediments employing chemical extractants. *The Science of the Total Environment*, Vol.17, pp: 165–196. doi:10.1016/0048-9697(81)90182-0.
- Lwanga, M. S.; Kansiime, F.; Denny, P.; Scullion, J., 2003. Heavy metals in Lake George, Uganda with relation to metal concentrations in tissues of common fish species. *Hydrobiologia*, Vol. 499 (1-3), pp: 83-93.
- Maher, W. A., & Aislabie, J., 1992. Polycyclic aromatic hydrocarbons in near shore marine sediments of Australia. *Science of Total Environment*, Vol. 112(2–3), pp: 143–164.
- Manta, D.S., Angelone, M., Bellanca, A., Neri, R., Sprovieri, M., 2002. Heavy metals in urban soils: a case study from the city of Palermo (Sicily), Italy. *The Science of the Total Environment*. Vol. 300 (1-3), pp: 229-243.

Maret Wolfgang, Sandstead Harold H., 2005. "Zinc requirements and the risks and benefits of zinc supplementation". *Journal of Trace Elements in Medicine and Biology*, Vol. 20, pp: 3-18.

Marschner, H., 1995. Mineral nutrition of higher plants, Academic Press, London.

- Martin, J.A.R.G., Arias, M.L.P., Corb, J.M.G., 2006. Heavy metal contents in agricultural topsoils in the Ebro basin (Spain). Application of the multivariate geoestatistical methods to study spatial variations. *Environmental Pollution*. Vol. 144. pp: 1001-1012.
- Martin, J. M. and Whitfield, M.: 1983, 'The significance of the river input of chemical elements to the ocean', in C. S.Wong, E. Boyle, K.W. Bruland, J. D. Burton and E. D. Goldberg (eds.), *Trace Metals in Sea Water*, Plenum Press, New York.
- McCready, S., Birch, G., & Long, E., 2006. Metallic and organic contaminants in sediments of Sydney Harbour, Australia and vicinity—a chemical dataset for evaluating sediment quality guideline. *Environmental International*, 32, 455– 465.
- McMurry, J. and R.C. Fay, 2004. Hydrogen, Oxygen and Water. In: McMurry Fay Chemistry. K.P. Hamann, (Ed.). 4th Edn. New Jersey: Pearson Education, pp: 575-599.
- Mendie, U., 2005. The Nature of Water. In: The Theory and Practice of Clean Water Production for Domestic and Industrial Use. Lagos: Lacto-Medals Publishers, pp: 1-21.
- Meza-Figueroa, D., Maier, R. M., de la O-Villaneuva, M., Gomez-Alvarez, A., Moreno-Zazueta, A., Rivera, J., et al., 2009. The impact of unconfined mine tailings in residential areas from a mining town in a semi-arid environment: Nacozari, Sonora, Mexico. *Journal Chemosphere*, Vol. 77(1), pp: 140 – 147.
- Mico, C., Recatala, L., Peris, M., and Sanchez, J., 2006. Assessing heavy metal sources in agricultural soil of an European Mediterranean area by multivariate analysis. *Chemosphere*, Vol. 65. pp: 863-872.
- Middelburg, J. J., & Soetaert, K., 2004. The role of sediment in shelf ecosystem dynamics. In J. M. Allan, R. Robinson, & B. J. Rothschild (Eds.), The sea, Vol. 13, pp. 353–373. Boston: President and Fellows of Harvard College.
- Mills C.F., 1986. "The Influence of Chemical Species on the Adsorption and Physiological Utilization of Trace Elements from the Diet or Environment". From the report of the Dahlem Conference: The Importance of Chemical Speciation in Environmental Processes. Editor: Bernhard M. Springer-Verlag.
- Mishra, V.K., Kim, K.H., Hang, C. H., & Choi, K. C., 2004. Wintertime sources and distribution of airborne lead in Korea. *Journal Atmospheric Environment*, Vol. 38(17), pp: 2653-2664. doi:10.1016/j.atmosenv.2004.02.025.

- Moreira, H., Marques, A.P.G.C., Rangel, A.O.S.S., & Castro, P.M.L., 2011. Heavy metal accumulation in plant species indigenous to a contaminated Portuguese site: prospects for phytoremediation. *Water Air Soil Pollut*, Vol. 221, pp: 377-389. doi: 10.1007/s11270-011-0797-6.
- Morgan, J.J. and Stumm, W., 1964. The role of multivalent metal oxides in limnological transformations as exemplified by iron and manganese. *Water Pollutant Control Feder.*, Vol. 36, pp: 276-277.
- Morrilo, J., Usero, J., & Garcia, I., 2002. Partitioning of metals in sediments from the Odiel River (Spain). *Environment International*, Vol. 28. pp: 263-271.
- Morillo J, Usero J, Gracia I., 2004. Heavy metal distribution in marine sediments from the southwest coast of Spain. *Chemosphere*, Vol. 55. pp: 431–442.
- Morillo, J., Usero, J., & Gracia, I., 2007. Potential mobility of metals in polluted coastal sediments in two Bays of Southern Spain. *Journal of Coastal Research*. Vol. 23. pp:352–361.
- Morton, B, Blackmore, G., 2001. South China Sea. *Marine Pollution Bulletin*, Vol. 42, pp: 1236-1263.
- Mohiuddin, K. M.; Zakir, H. M.; Otomo, K.; Sharmin, S.; Shikazono, N., 2010. Geochemical distribution of trace metal pollutants in water and sediments of downstream of an urban river. *Int. J. Environ. Sci. Tech.* Vol. 7 (1). pp: 17-28.
- Mohiuddin, K.M., Ogawa, Y., Zakir, H.M. Otomo, K. & Shikazono, N., 2011. Heavy metals contamination in water and sediments of an urban river in a developing country. *Int. J. Environ. Sci. Tech.*, Vol. 8 (4). pp: 723-736. ISSN 1735-1472.
- Mountouris, A., Voutsas, E., Tassios, D., 2002. Bioconcentration of heavy metals in aquatic environments: the importance of bioavailability. *Marine Pollution Bulletin*, Vol. 44, pp: 1136-1141.
- Mucha, A. P., Vasconcelos, M. T. S. D., & Bordalo, A. A., 2003. Macrobenthic community in the Doura estuary: Realtionship with trace metals and natural sediment characteristics. *Journal Environmental Pollution*, Vol. 121, pp: 169 – 180.
- Mudge, S.M., Duce, C.E., 2005. Identifying the source, transport path and sink of sewage derived organic matter. *Journal Environmental Pollution*, Vol. 136, pp: 209-220.
- Müller U., 2007. Inorganic Structural Chemistry. John Wiley, Chichefster
- Munch Christensen, A., Nakajima, F. & Baun, A., 2006. Toxicity of water and sediment in a small urban river (Store Vejlea, Denmark). *Environmental Pollution*, Vol. 144, pp: 621-625.

- Munuz BA, Gutierrez GE, Segovia ZJ, Delgadillo HF, Sandoval SG., 2004. Trace metal enrichment in surficial sediments of the northern coast of Baja California, Mexico. *Mar Pollut Bull*. Vol. 48. pp:587–603.
- Nasrabadi, T., Bidhendi, G.N., Karbassi, A., & Mehrdadi N., 2010. Evaluating the efficiency of sediment metal pollution indices in interpreting the pollution of Haraz River sediments, Southern Caspian Sea basin. *Environ Monit Assess*. Vol. 171. pp: 395-410.
- NAS., 1977b. Arsenic. Drinking water and health. Washington, DC: National Academy of Sciences, Vol. 316-344, pp: 428-430.
- Nicholson, F.A., Smith, S.R., Alloway, B.J. Carlton-Smith, C., Chambers, B.J., 2003. An inventory of heavy metals inputs tp agricultural soil in England and Wales. *Sci. Total Environ.* Vol. 311. pp: 205-219.
- Newman, Alan., 1996. "Elements of ICPMS." *Analytical Chemistry*. Vol.68(Jan 1), pp: 46A-51A.
- Nriagu, J. O., 1979. Global inventory of natural and anthropogenic emissions of trace metals to the atmosphere. Nature, Vol. 279, pp: 409–411.
- Nriagu, J.O., 1988. A silent epidemic of environmental metal poisoning. *Environ. Pollut.*, Vol. 50, pp: 139-161.
- Nriagu JO, Pacyna JM., 1988. Quantitative assessment of worldwide contamination of air, water and soils by trace metals. *Nature*, Vol. 333, pp: 134-139.
- Nyarco, B.J.B., Serfor-Armah, Y., Akaho, E.H.K., Adomako, D., Pasae, S. 2004. Determination of heavy metal pollution levels in lichens at Obuasi gold mining area in Ghana. J. Apply Sci Technol, Vol. 9 (1-2), pp: 28 – 33.
- Nyarco, B.J.B., Adomako D, Serfor-Armah, Y, Dampare, S.B., Adotey, D.K., Akaho E.H.K. 2006. Biomonitoring of atmospheric trace element deposition around an industrial town in Ghana. Radiat Phys Chem, Vol. 75 (9), pp: 954-958.
- OECD Declaration on risk reduction for lead. Adopted at the meeting of Environment Ministers, February 20, 1996.
- Oehme, F.W. (ed). 1979. Toxicity of Heavy Metals in the Environment Part II. Marcel Dekker, Inc. New York/Basel.
- Ochieng EZ, Lalah JO, Wandiga SO., 2006. Heavy metals in water and surface sediment in Winam Gulf of lake Victoria, Kenya. *Bull. Environ. Contam. Toxicol.* Vol. 77. pp: 459-468. doi. 10.1007/s00128-006-1087-7.

- Ochieng EZ, Lalah JO, Wandiga SO., 2007. Analysis of Heavy Metals in Water and Surface Sediment in Five Rift Valley Lakes in Kenya for Assessment of Recent Increase in Anthropogenic Activities. *Bull. Environ. Contam. Toxicol*, Vol. 79. pp: 570-576. doi. 10.1007/s00128-007-9286-4.
- Okafor, E. Ch., Opuene, K., 2007. Preliminary assessment of trace metals and polycyclic aromatic hydrocarbons in the sediments. *Int. J. Environ. Sci. Tech.*, Vol. 4 (2). pp: 233-240.
- Olesik, John W., 1996. "Fundamental Research in ICP-OES and ICPMS." Analytical Chemistry. Vol. 68(Aug 1), pp: 469A-474A
- Olofsson, I., 2002. Kartläggning och provtagning av Lövskataviken och Inre Skurholmsfjärden. 2002:299. Avd. för Tillämpad Geologi. Luleå, Luleå University of Technology.
- Olsgard, F., 1999. Effects of copper contamination on recolonisation of subtidal marine soft sediments—an experimental field study. *Mar. Pollut. Bull.* Vol. 38, pp: 448–462.
- Owens PN, Batalla RJ, Collins AJ, Gomez B, Hicks DM, Horowitz AJ, Kondolf GM, Marden M, Page MJ, Peacock DH, Petticrew EL, Salomons W, Trustrum NA., 2005. Fine-grained sediment in river systems: Environmental significance and management issues. *River Res Appl*, Vol. 21, pp: 693-717.
- Pacyna JM, Scholtz MT, Li Y-F., 1995. Global budget of trace metal sources. *Environ Rev*, Vol. 3(2), pp: 145-159.
- Panda, U.C., Sundaray, S.K., Rath, P., Nayak, B.B., Bhatta, D., 2006. Application of factors and cluster analysis for characterization of river and estuarine water systems-a case study; Mahanadi River (India). J. Hydrol, Vol. 331, pp: 434-445.
- Park, D., Yun, Y. S., Jo, J. H., & Park, J. M., 2006. Biosorption process for treatment of electroplating wastewater containing Cr(VI): Laboratory-scale feasibility test. *Industrial and Engineering Chemistry Research*, Vol. 45, pp: 5059–5065.
- Pekey, H., 2006. The distribution and sources of heavy metals in Izmit Bay surface sediments affected by a polluted stream. *Marine Pollution Bulletin*, Vol. 52, pp: 1197–1208
- Pertsemli, E., & Voutsa, D., 2007. Distribution of heavy metals in Lakes Doirani and Kerkini, Northern Greece. *Journal of Hazardous Materials*, Vol. 148(3), pp: 529-537.
- Peters SC, Blum JD, Klaue B, et al., 1999. Arsenic occurrence in New Hampshire drinking water. *Environ Sci Technol*, Vol. 33, pp: 1328-1333.

- Petrovic, S., Semencic, L., Ozretic, B. and Ozretic, M., 2004. Seasonal Variation of Physicological and Cellular Biomarkers and Their Use in The Biomonitoring of North Adriatic Coastal Waters (Croatia). *Marine Pollution Bulletin* 49(9-10): 713-720.
- Qadir, A., Malik, R. N., & Husain, S. Z., 2007. Spatio-temporal variations in water quality of Nullah Aik-tributary of the river Chenab, Pakistan. *Journal Environmental Monitoring and Assessment*, Vol. 140(1–3), pp. 43–59. doi:10.1007/s1066100798464.
- Qu, W. and Kelderman, P., 2001. 'Heavy metal contents in the delft canal sediments and suspended solids of the river rhine: multivariate analysis for source tracing', *Chemos.* Vol. 45, pp: 919–925.
- Radakovitch, O., Roussiez, V., Ollivier, P., Ludwig, W., Grenz, C., & Probst, J., 2008. Input of particulate Heavy Metals from Rivers and Associated Sedimentary Deposits on The Gulf of Lion Continental Shelf. *Estuarine, Coastal and Shelf Science*, Vol. 77, pp: 285-295.
- Raj MR and Jayaprakash M., 2008. Distribution and enrichment of trace metals in marine sediments of Bay of Bengal, off Ennore, south-east coast of India. *Journal Environ Geo*, Vol.56. pp:207–217. doi. 10.1007/s00254-007-1156-1.
- Ramos et al., 1994 L. Ramos, L.M. Hernandez and M.J., 1994. Gonzalez, Sequential fraction of copper, lead, cadmium and zinc in soils from or near Donana National Park. *Journal of Environmental Quality*, Vol. 23, pp: 50–57.
- Reid, M.K. and Spencer, K.L., 2009. Use of principal components analysis (PCA) on estuarine sediment datasets: The effect of data pre-treatment. *Journal Environmental Pollution*, Vol. 157, pp: 2275-2281.
- Renzt, R., Widerlund, A., Viklander, M., and Ohlander, B., 2011. Impact of urban stromwater on sediment quality in an Enclosed Bay of the Lule River, Northern Sweeden. *Journal Water Air Soil Pollut*. Vol. 218, pp: 651–666. doi: 10.1007/s11270-010-0675-7.
- Rilley, C., 1980. Metal contamination of food. Applied Science Publisher, London.
- Rubio, B., Pye, K., Rae, J. E., & Rey, D., 2001. Sedimentological characteristics, heavy metal distribution and magnetic properties in subtidal sediments, Ria de Pontevedra, NWSpain. *Sedimentology*, Vol. 48, pp: 1277–1296.
- Salanki, J., Licsko, I., Laszlo, F., Balogh, K.V., Varanka, I., and Mastala, Z., 1992. Changes in the concentration of heavy metals in the Zala Minor Balaton-Zala system (Water, Sediment, Aquatic Life). *Water Sci. Technol.*, Vol. 25, pp: 173-180.

Salomons, W., & Forstner, U., 1984. Metal in Hydrocycle. New York: Springer.

- Salomons, W., & Fo[°]rstner, U., 1984. *Metals in the Hydrocycle*. Springer-Verlag, Berlin.
- Salati, S. and Moore, F., 2010. Assessment of heavy metal concentration in the Khoshk River water and sediment, Shiraz, Southwest Iran. *Journal Environ Monit Assess*, Vol. 164, pp: 677-689. doi:10.1007/s10661-009-0920-y.
- Sampson M. L., Bostick B., Chiew H., Hagan J. M. and Shantz A., 2008. Arsenicosis in Cambodia: Case studies and policy response. *Apll. Geochem.* Vol. 23, pp: 2977– 2986.
- Santos, I. R., Silva, E. V., Schaefer, C. E. G. R., Albuquerque, M. R., & Campos, L. S., 2005. Heavy metal contamination in coastal sediments and soils near the Brazilian Antarctic Station, King George Island. *Marine Pollution Bulletin*, Vol. 50, pp: 185–194
- Schiff, K. C., & Weisberg, S. B. (1999). Iron as a reference element for determining trace metal enrichment in Southern California coast shelf sediments. *Journal Marine Environmental Research*, 48, 161-176
- Schwarzbauer, J., & Ricking, M., 2010. Non-target screening analysis of river water as compound related base for monitoring measures. Environmental Science and Pollution Research, Vol. 17, pp: 934–947.
- Shakeri, A., & Moore, F., 2010. The impact of an industrial complex on freshly deposited sediments, Chener Rahdar river case study, Shiraz, Iran. *Environ Monit Assess.* Vol. 169. pp: 321-334. doi: 10.1007/s10661-009-1173-5.
- Shea EE., 1996. Lead regulation handbook. Rockville, MD: Government Institutes.
- Shekabira, K., Origa, H.O., Basamba, T.A., Mutumba, G., and Kakudidi, E., 2010. Assessment of heavy metal pollution in the urban stream sediments and its tributaries. *Int. J. Environ. Sci. Tech.*, Vol. 7 (3). pp: 435-446, Summer 2010. ISSN: 1735-1472.
- Sherameti and A. Varma (eds.), *Soil Heavy Metals*, Soil Biology, Vol 19, DOI 10.1007/978-3-642-02436-8_2, © Springer-Verlag Berlin Heidelberg 2010.
- Shresta, S., Kazama, F., 2007. Assessment of surface water quality using multivariate statictical techniques in hydrogeochemical studies: an example from Karnataka, India. *Journal Water Res*, Vol. 36, pp: 2437-2442.
- Shin, P.K.S., Lam, W.K.C., 2001. Development of a marine sediment pollution index, *Journal Environmental Pollution*, Vol. 113, pp: 281-291.
- Simeonov, V., Massart, D. L., Andreev, G. and Tsakovski, S., 2000. 'Assessment of metal pollution based on multivariate statistical modeling of 'hot spot' sediments from the black sea', *Chemos.* Vol. 41, pp: 1411–1417.
- Simeonov, V., Stanimirova, I., & Tsakovski, S., 2001. Multivariate statistical interpretation of coastal sediment monitoring data. *Fresenius' Journal of Analytical Chemistry*, Vol. 370, pp: 719–722.
- Simmons, I. G., 1991. Earth, air, and water: resources and environment in the late 20th century. London, UK: Edward Arnold
- Sin, S. N., Chua, H., Lo, W. and Ng, L. M., 2001. Assessment of heavy metal cations in sediments of Shing Mun River, Hong Kong. *Environment International*, Vol. 26, pp: 297-301.
- Smith, L.A., Means, J.L., Chen, A., Alleman, B., Chapman, C.C., Tixier, J.S., Jr., et al., 1995, *Remedial Options for Metals-Contaminated Sites*. Boca Raton, FL: Lewis Publishers.
- Soares, H.M.V.M., Boavebtura, R.A.R., Machado, A.A.S.C., and Silva, J.C.G.E., 1999. *Environmental Pollution*, Vol. 105, pp: 311-323.
- Song, Y-H, Peng, J-F, Yuan, P., Cui, X-Y, Qiu, G-L. 2009. The remediation of heavy metals contaminated sediment, *Journal of Hazardous Material*, Vol. 161, pp: 633-640.
- Srinivasa Reddy, M., Shaik Basha, Sravan Kumar, V.G., Joshi, H.V., Ghosh, P.K., 2003. Quantification and classification of ship scraping waste at Alang–Sosiya, India. *Journal Marine Pollution Bulletin*, Vol. 46, pp: 1609–1614.
- Stoeppler, M., 1992. Hazardous Metals in the Environment. Amsterdam: Elsevier., J.
- Sutherland CA, Milner EF., 1990. Lead. In: Elvers B, Hawkins S, Schulz G, eds. Ullmann's encyclopedia of industrial chemistry. 5th edition. New York, NY: VCH Publishers, 193-236
- Tamaki S, Frankenberger WT., 1992. Environmental biochemistry of arsenic. *Rev Environ Contam Toxicol*, Vol. 124, pp: 79-110.
- Thornton I., 1992. Sources and pathways of cadmium in the environment. *IARC Sci Publ*, Vol. 118, pp: 149-162.
- Tokalioglu, S., Kartal, S., & Elçi, L., 2000. Determination of heavy metals and their speciation in lake sediments by flame atomic absorption spectrometry after a four-stage sequential extraction procedure. *Analytica Chimica Acta*, Vol. 413(1–2), pp: 33–40.
- Tomlinson, D.L., Wilson, J.G., Harris, C.R., and Jefrfrey, D.W. 1980. Problems in the assessments of heavy metal levels in eastuaries and formation of pollution index. Helgol Meeresunters, Vol. 33, pp. 566-575.
- Tsuji, L. J. S.; Karagatzides, J. D., 2001. Chronic lead exposure, body condition and testis mass in wild Mallard Ducks, B.

- Turekian, K. K., & Wedepohl, K.H. (1961). Distribution of the elements in some major units of the earth's crust. Bulletin of Geological Society of America, 72, 175– 192.
- Turner, R.E., 2001. Of manatees, mangroves, and the Mississippi Paleo-indicators in Charlotte Harbor 533. River: Is there an estuarine signature for the Gulf of Mexico? Estuaries, Vol. 24: pp: 139–150.
- Turner, A., Millward, G.E., 2002. Suspended particles: their role in estuarine biogeochemical cycles, Estuary. *Coast. Shelf Sci.* Vol. 55, pp: 857–883.
- Tusseau-Vuillemin, M. H., Gourlay, C., Lorgeoux, C., Mouchel, J.-M., Buzier, R., Gilbin, R., et al., 2007. Dissolved and bioavailable contaminants in the Seine river basin. *The Science of the Total Environment*, Vol. 375, pp: 244–256.
- Uluozlu, O. D., Sari, A., Tuzen, M., & Soylak, M. 2008. Biosorption of Pb(II) and Cr(III) from aqueous solutions by lichen (Parmelina tiliaceae) biomass. *Bioresourc Technology*, Vol. 99, pp: 2972–2980.
- Uria AF, Mateo, C.L., Roca, E., and Marcos, M.L.S., 2009. Source identification of heavy metals in pastureland by multivariate analysis in NW Spain. *Journal Hazardous Materials*, Vol. 165. pp: 1008-1015.
- USEPA US Environmental Protection Agency. 1998. Report of the federal advisory committee on the total maximum daily load (TMDL) program: The national advisory council for environmental policy and technology. EPA 100-R-98-006. Office of the Administrator, Washington, DC, USA. (12).
- USGS., 1997. Minerals yearbook: Cadmium. U. S. Geological Survey, Reston, Virginia.
- Vald'es, J., Vargas, G., Sifeddine, A., Ortlieb, L., & Guinez, M., 2005. Distribution and enrichment elevation of heavy metals in Mejillones Bay (23°S), Northern Chile: Geochemical and statistical approach. *Marine Pollution Bulletin*, Vol. 50. pp: 1558-1568.
- Valdes, J., Roman, D., Guinez, M., Rivera, L., Morales, T., Avila, J., and Cortes, P., 2010. Distribution and temporal variation of trace metal enrichment in surface sediments of San Jorge Bay, Chile. J. Environ Monit Assess. Vol. 167. pp: 185-197.
- Vaalgamaa, S and Conley, D. J., 2008. Detecting environmental change in estuaries: Nutrient and heavy metal distributions in sediment cores in estuaries from the Gulf of Finland, Baltic Sea. *Estuarine, Coastal and Shelf Science*, Vol. 76, pp: 45-56.
- Valentukevičienė M. and Brannvall E., 2008. Marine pollution: an overview. *Geologija*. *Vilnius*. Vol. 1(61), pp: 17–23.
- Vanloon, G.W. and S.J. Duffy., 2005. The Hydrosphere. In: Environmental Chemistry: A Global Perspective. 2nd Edn. New York: Oxford University Press, pp: 197-211.

- Varol M and Sen B., 2009. Assessment of surface water quality using multivariate statistical techniques: a case study of Behrimaz Stream, Turkey. J. Environ Monit Assess. Vol.159. pp. 543-553. doi: 10.1007/s10661-008-0650-6.
- Vazquez, A., M.Costoya, R.M Pena., S.Garcia, and C.Herrero., 2003. A rainwater quality monitoring network: a preliminary study of the composition of rainwater in Galicia (NW Spain). *Chemosphere*. Vol. 51, pp: 375–386
- Vdovic, N., Billon, G., Gabelle, C., Wartel, M., & Potdevin, J.-L., 2006. Remobilization of metal from slag and polluted sediments (case study: the River Deule Canal, North of Frace). *J. Environmental Pollution*, Vol. 141, pp: 359-369.
- Vega M.,Pardo R., Barrado E, Deban L., 1998. Assessment of seasonal and polluting effects on the quality or river water by exploratory data analysis. *Journal Water Res*, Vol. 32, pp: 3581-3592.
- Vukovic, Z., Radenkovic, M., Stankovic, S.J., Vukociv, D., 2011. Distribution and accumulation heavy metals in the water and sediments of the River Sava. J. Serb. Chem. Soc. Vol. 76 (5). pp: 795-803. JSCS-4160.
- Wahlberg, J.E., 1965. Percutaneous toxicity of metal compounds A comparative investigation in guinea-pigs. Arch. Environ. Health, Vol. 11, pp: 201-204.
- Wagner, A., & Boman, J., 2003. Biomonitoring of trace elements in muscle and liver tissue of freshwater fish. Spectrochimica Acta Part B, Vol. 58, pp: 2215–2226.
- Walling, D.E., & Fang, D., 2003. Recent trends in the suspended sediments loads of the world's rivers. *Global and Planetary Change*, Vol. 39. pp: 111 – 126.
- Wang, L. and Wu, J., 2008. Spatial variability of heavy metals in soil across a valley plain in Southeastern China. *Journal Environ Geol*, Vol. 55, pp: 1207-1217.
- Warren, L. J., 1981, 'Contamination of sediments by lead, zinc and cadmium A review', *Environ. Pollut.* 2, Ser. B 401–436.
- Waters, T.F., 1995. Sediment in streams: Sources, Biological effect and control. American Fisheries Society.
- Webb, M., 1975. Metallothionein and toxicity of Cd: Proc. Of NATO Sci. Conf. on Ecotoxicol. Res. Effects of heavy metals and organohalogen compounds (pp. 177–186). NY: Plenum Press.
- Wildi, W., Dominik, J., Loizeau, J., Thomas, R. L., Favarger, P., Haller, L., Perroud, A. & Peytremann, C., 2004. River, reservoir and lake sediment contamination by heavy metals downstream from urban areas of Switzerland. *Lakes & Reservoirs: Research and Management*, Vol. 9, pp: 75-87.
- WHO., 2003, "Arsenic in Drinking Water," available at <u>http://www.who.int/water</u> sanitation_health/dwq/chemicals/arsenic.pdf (last visited Nov. 19, 2010).

- Wood PJ, Armitage PD., 1997. Biological effects of fine sediment in the lotic environment. *Environ Manag*, Vol. 21, pp: 203-217.
- Wooley, J., & Kvech, S., 2011. ICP-MS. <u>http://www.cee.vt.edu/ewr/environmental/teach/smprimer/icpms/icpms.htm</u> (last access 2011).
- Worthy, Ward., 1988. "Scope of ICP/MS expands to many fields." *Chemical and Engineering News*. Vol. 66(June 27), pp: 33-4.
- Yalcin, M. G., Aydin, O., & Elhatip, H., 2008. Heavy metal contents and the water quality of Karasu Creek in Nigde, Turkey. *Environmental Monitoring and Assessment*. Vol. 137. pp: 169-178.
- Yang, Z.F., Wang, Y., Shen, Z. Y., Niu, J.F., Tang, Z. W., 2009. Distribution and Specification of Heavy Metals in Sediments from the Mainstream, Tributaries, and Lakes of The Yangtze River catchment of Wuhan, China. *Journal of Hazardous Materials*, Vol. 166, pp: 1186-1194.
- Yang, Z., Lu, W., Long, Y., Bao, X., and Yang, Q., 2011. Assessment of heavy metals contamination in urban topsoil from Changcun City, China. *Journal Geochemical Exploration*. Vol. 108. pp:27-38.
- Yap, C.K. & Pang, B.H., 2011. Assessment of Cu, Pb, and Zn contamination in sediment north western Peninsular Malaysia by using sediment quality western and different geochemical indices. *Environ Monit Assess.* Vol. 183. pp: 23-39.
- Yawei, W., Lina, L., Jianbo, S., Guibin, J., 2005. Chemometrics methods for the investigation of methylmercury contamination in mollusks samples collected from coastal sites along the Chinese Bohai Sea, *Journal Environmental Pollution*, Vol. 135, pp: 457-467.
- Yin, H., Deng, J., Shao, S., Gao, F., Gao, J., and Fan, C., 2010. Distribution characteristics and toxicity assessment of heavy metals in the sediments of Lake Chaohu, China. *Environ Monit Assess*. doi: 10.1007/s10661-010-1746-3
- Yongming, H., Peixuan, D., Junji, C., & Posmentier, E. S., 2006. Multivariate analysis of heavy metal concentration in urban dust of Xi'an, Central China. *The Science of the Total Environment*, Vol. 355, pp: 176-118.
- Yu, K. Y., Tasi, L. J., Chen, S. H., & Ho, S. T., 2001. Chemical binding of heavy metals in anoxic river sediments. *Water Research*. Vol. 35(7). pp: 4086–4094.
- Yuan Y., Marshall G., Ferreccio C., Steinmaus C., Selvin S., Liaw J., Bates M.N. and Smith A. H., 2007. Acute myocardial infarction mortality in comparison with lung and bladder cancer mortality in arsenic-exposed region II of Chile from 1950 to 2000. Am. J. Epidemiol. Vol. 166, pp: 1381–1391
- Yunice, A.A., Perry, E.F., and Perry, H.M., 1968. Effect of desferrioxamine on trace in rat organs. *Arch. Environ. Health*, Vol. 16, pp: 163-170.

- Yun Y-S, Park D, Park JM, Volesky B., 2001. Biosorption of trivalent chromium on the brown seaweed biomass. Environ Sci Technol. Vol. 35, pp: 4353–4358.
- Zabetoglou, K., Voutsa, D., & Samara, C., 2002. Toxicity and heavy metal contamination of surficial sediments from the Bay of Thessaloniki (Northwestern Aegean Sea) Greece. *J. Chemosphere*, Vol. 49. pp:17–26.
- Zhou, H.Y., Peng X.T., Pan, J.M., 2004. Distribution, source and enrichment of some chemical elements in sediments of the Pearl River Estuary, China. *Cont. Shelf Res*, Vol. 24, pp: 1857 – 1875.
- Zhang, C., 2006. Using multivariate analyses and GIS to identify pollutants and their spatial patterns in urban soils in Galway, Ireland. *Environmental Pollution*, Vol. 142, pp: 502-511.
- Zhang, L., Ye, X., Feng, H., Jing, Y., Ouyang, T., Yu, X., et al., 2007. Heavy metal contamination in western Xiamen Bay sediments and its vicinity, China. *Marine Pollution Bulletin*, Vol. 54, pp: 974–982
- Zhang MY, Cui LJ, Sheng LX, Wang YF., 2009. Distribution and enrichment of heavy metals among sediments, water body and plants in Hengshuihu Wetland of Northern China. J. Ecol. Eng. Vol. 35. pp: 563–569.
- Zhang H, Cui B, Xiao R, Zhao H., 2010. Heavy metals in water, sediment and plant in riparian wetlands in the Pearl River Estuary, South China. *Procedia Environmental Sciences*. Vol 2. pp. 1344-1354.

The average of heavy metals concentrations in sediment Balok River (ppm) of three sampling points

AVERAGE OF HEAVY METALS CONCENTRATION IN SEDIMENT OF THREE SAMPLING POINT BALOK RIVER											
Location	Month	Al	Cr	Mn	Fe	Ni	Cu	Zn	As	Cd	Pb
	Nov-10	2698.133	4.553	14.053	2735.073	1.553	1.233	7.043	1.040	0.213	10.093
Location 1	Mar-11	10169.028	7.822	23.121	6024.462	2.652	2.253	7.004	3.094	0.152	11.664
	Jul-11	9478.373	6.459	28.814	8180.969	2.049	3.104	5.459	2.830	0.187	9.146
	Sum	22345.535	18.835	65.988	16940.505	6.255	6.590	19.506	6.964	0.552	30.903
	mean	7448.512	6.278	21.996	5646.835	2.085	2.197	6.502	2.321	0.184	10.301
	std	4128.416	1.642	7.444	2742.517	0.550	0.937	0.904	1.117	0.031	1.272
	Nov-10	3819.933	8.583	6.273	2376.023	3.583	1.883	9.143	0.693	0.053	2.243
Location 2	Mar-11	15619.032	14.812	35.174	7735.464	3.053	6.663	16.701	2.314	0.163	12.034
Location 2	Jul-11	13233.512	14.406	31.009	6117.801	2.283	8.507	19.186	3.114	0.245	9.667
	Sum	32672.477	37.801	72.456	16229.289	8.919	17.053	45.030	6.121	0.461	23.944
	mean	10890.826	12.600	24.152	5409.763	2.973	5.684	15.010	2.040	0.154	7.981
	std	6238.655	3.485	15.623	2748.980	0.654	3.418	5.230	1.233	0.096	5.108
		Al	Cr	Mn	Fe	Ni	Cu	Zn	As	Cd	Pb
	Nov-10	4922.78	13.85	11.247	4527.657	2.677	4.797	8.727	1.027	1.497	7.057
Location 3	Mar-11	12379.02767	16.694	26.522	7478.463	2.659	6.267	16.032	2.428	0.149	15.818
	Jul-11	14412.86333	17.302	24.554	8412.856	3.026	4.629	15.050	2.892	0.203	22.162
	Sum	31714.671	47.846	62.322	20418.976	8.361	15.693	39.809	6.347	1.849	45.037
	mean	10571.557	15.949	20.774	6806.325	2.787	5.231	13.270	2.116	0.616	15.012
	std 4996.562 1.843 8.309 2027.935 0.207 0.901 3.965 0.971 0.363 7.585										7.585

The average of heavy metals concentrations in sediment Balok River (ppm) during November 2010 until July 2011

AVE	AVERAGE OF HEAVY METALS CONCENTRATION IN SEDIMENT DURING NOVEMBER 2010 UNTIL JULY 2011											
Month	Location	Al	Cr	Mn	Fe	Ni	Cu	Zn	As	Cd	Pb	
	Loc 1	2698.133	4.553	14.053	2735.073	1.553	1.233	7.043	1.040	0.213	2698.133	
Nov-10	Loc 2	3819.933	8.583	6.273	2376.023	3.583	1.883	9.143	0.693	0.053	3819.933	
	Loc 3	4922.780	13.850	11.247	4527.657	2.677	4.797	8.727	1.027	1.497	4922.780	
	Sum	11440.847	26.987	31.573	9638.753	7.813	7.913	24.913	2.760	1.763	11440.847	
	mean	3813.616	8.996	10.524	3212.918	2.604	2.638	8.304	0.920	0.588	6.464	
	std	1112.331	4.662	3.940	1152.663	1.017	1.898	1.112	0.196	0.291	3.958	
	Loc 1	10169.028	7.822	23.121	6024.462	2.652	2.253	7.004	3.094	0.152	11.664	
Mar-11	Loc 2	15619.032	14.812	35.174	7735.464	3.053	6.663	16.701	2.314	0.163	12.034	
Mar-11	Loc 3	12379.028	16.694	26.522	7478.463	2.659	6.267	16.032	2.428	0.149	15.818	
	Sum	38167.087	39.328	84.817	21238.390	8.364	15.183	39.737	7.836	0.464	39.516	
	mean	12722.362	13.109	28.272	7079.463	2.788	5.061	13.246	2.612	0.155	13.172	
	std	2741.176	4.674	6.214	922.650	0.229	2.440	5.416	0.421	0.008	2.299	
	Loc 1	9478.373	6.459	28.814	8180.969	2.049	3.104	5.459	2.830	0.187	9.146	
Jul-11	Loc 2	13233.512	14.406	31.009	6117.801	2.283	8.507	19.186	3.114	0.245	9.667	
	Loc 3	14412.863	17.302	24.554	8412.856	3.026	9.260	15.050	2.892	0.203	22.162	
	Sum	37124.749	38.167	84.376	22711.627	7.358	20.870	39.695	8.835	0.635	40.975	
	mean	12374.916	12.722	28.125	7570.542	2.453	6.957	13.232	2.945	0.212	13.658	
	std	2576.856	5.614	3.282	1263.442	0.510	3.358	7.042	0.150	0.030	7.369	

AVERAGE OF HEAVY METALS CONCENTRATION IN WATER OF THREE SAMPLING POINT BALOK RIVER										IVER	
Location	Month	Al	Cr	Mn	Fe	Ni	Cu	Zn	As	Cd	Pb
	15-Nov-10	0.484	0.001	0.044	229.812	0.043	0.168	0.094	0.014	0.034	0.024
	13-Mar-11	2.654	0.442	0.332	248.217	0.044	0.174	4.293	0.213	0.252	0.303
	06-Jul-11	3.129	0.372	0.173	154.596	0.071	0.117	2.629	0.171	0.037	0.017
Location 1	04-Jul-12	0.546	5.025	0.158	163.885	0.502	0.129	0.462	0.268	0.010	0.862
	13-Sep-12	1.661	0.274	0.110	156.475	0.106	0.095	3.715	0.166	0.020	1.164
	06-Oct-12	1.028	0.323	0.268	167.239	0.207	0.129	4.832	0.010	0.012	0.735
	8-Nov-12	0.804	0.408	0.157	163.885	0.145	0.302	4.292	0.045	0.043	1.032
	Sum	11.007	6.845	1.241	1284.109	1.118	1.114	20.317	0.887	0.159	4.137
	mean	1.572	0.978	0.177	183.444	0.160	0.159	2.092	0.127	0.022	0.591
	std	0.168	0.162	0.102	59.907	0.032	0.031	1.224	0.105	0.009	0.066
			ŀ								
	15-Nov-10	0.896	0.059	0.114	231.109	0.009	0.171	0.086	0.013	0.001	0.033
	13-Mar-11	4.304	0.174	0.184	124.833	0.039	0.168	0.924	0.249	0.152	0.293
	06-Jul-11	5.140	0.157	0.163	152.077	0.028	0.282	0.543	0.272	0.114	0.034
т. <i>с</i> : о	04-Jul-12	0.797	0.156	0.188	152.642	0.499	0.117	2.583	0.069	0.007	0.208
Location 2	13-Sep-12	1.824	0.368	0.079	188.520	0.108	0.109	2.079	0.174	0.008	0.421
	06-Oct-12	1.215	0.412	0.187	152.642	0.209	0.068	2.138	0.012	0.028	3.854
	8-Nov-12	0.764	0.394	0.099	200.041	0.212	0.215	4.965	0.032	0.022	2.219
	Sum	14.940	1.719	1.013	1201.864	1.104	1.130	13.318	0.822	0.097	7.061
	mean	2.134	0.246	0.145	171.695	0.158	0.161	1.903	0.117	0.014	1.009
	std	1.153	0.046	0.080	62.943	0.098	0.124	0.831	0.095	0.016	0.546

The average of heavy metals concentrations in water Balok River (ppm) of three sampling points

	15-Nov-10	1.653	0.032	0.081	235.701	0.034	0.052	0.142	0.023	0.004	0.043
	13-Mar-11	1.233	0.053	0.115	409.827	0.042	0.171	0.523	0.251	0.004	0.091
	06-Jul-11	3.129	0.071	0.151	295.942	0.029	0.164	1.483	0.334	0.063	0.048
Location 3	04-Jul-12	0.846	0.213	0.530	156.809	0.719	0.143	4.467	0.405	0.166	2.971
Location 5	13-Sep-12	0.624	0.019	0.085	437.629	0.383	0.022	3.715	0.127	0.019	0.101
	06-Oct-12	0.351	0.035	0.201	172.681	0.212	0.379	2.460	0.152	0.012	1.557
	8-Nov-12	0.762	0.492	0.053	277.330	0.388	0.277	2.036	0.024	0.016	0.840
	Sum	8.598	0.915	1.217	1985.918	1.807	1.208	14.826	1.316	0.315	5.651
	mean	1.228	0.131	0.174	283.703	0.258	0.173	2.118	0.188	0.045	0.807
	std	0.626	0.094	0.085	187.780	0.045	0.214	0.743	0.057	0.107	0.026



AVERAGE OF HEAVY METALS CONCENTRATION IN WATER DURING NOV 2010 UNTIL NOV 2012											
Month	Location	Al	Cr	Mn	Fe	Ni	Cu	Zn	As	Cd	Pb
	Loc 1	0.484	0.001	0.044	229.812	0.043	0.168	0.094	0.014	0.034	0.024
Nov-10	Loc 2	0.896	0.059	0.114	231.109	0.009	0.171	0.086	0.013	0.001	0.033
	Loc 3	1.653	0.032	0.081	235.701	0.034	0.052	0.142	0.023	0.004	0.043
	Sum	3.033	0.092	0.240	696.622	0.086	0.391	0.322	0.050	0.039	0.100
	mean	1.011	0.031	0.080	232.207	0.029	0.130	0.107	0.017	0.013	0.033
	std	0.593	0.029	0.035	3.094	0.017	0.068	0.030	0.005	0.018	0.010
	Loc 1	2.654	0.442	0.332	248.217	0.044	0.174	4.293	0.213	0.252	0.303
Mar-11	Loc 2	4.304	0.174	0.184	124.833	0.039	0.168	0.924	0.249	0.152	0.293
Mar-11	Loc 3	1.233	0.053	0.115	409.827	0.042	0.171	0.523	0.251	0.004	0.091
	Sum	8.191	0.669	0.631	782.877	0.125	0.512	5.740	0.714	0.407	0.687
	mean	2.730	0.223	0.210	260.959	0.041	0.171	1.913	0.238	0.136	0.229
	std	1.537	0.199	0.111	142.923	0.003	0.003	0.271	0.021	0.125	0.119
	Loc 1	3.830	0.372	0.173	154.596	0.071	0.117	2.629	0.171	0.037	0.017
Jul-11	Loc 2	5.140	0.157	0.163	152.077	0.028	0.282	0.543	0.272	0.114	0.034
	Loc 3	3.129	0.071	0.151	295.942	0.029	0.164	1.483	0.334	0.063	0.048
	Sum	12.099	0.599	0.488	602.614	0.128	0.563	4.656	0.777	0.214	0.098
	mean	4.033	0.200	0.163	200.871	0.043	0.188	1.552	0.259	0.071	0.033
	std	1.021	0.155	0.011	82.343	0.025	0.085	1.045	0.083	0.039	0.015

The average of heavy metals concentrations in water Balok River (ppm) during November 2010 until November 2012

Month	Location	Al	Cr	Mn	Fe	Ni	Cu	Zn	As	Cd	Pb
	Loc 1	0.546	5.025	0.158	163.885	0.502	0.129	0.462	0.268	0.010	0.862
July-12	Loc 2	0.797	0.156	0.188	152.642	0.499	0.117	2.583	0.069	0.007	0.208
5	Loc 3	0.846	0.213	0.530	156.809	0.719	0.143	4.467	0.405	0.166	2.971
	Sum	2.189	5.349	0.875	473.336	1.720	0.389	7.512	0.742	0.183	4.041
	mean	0.730	1.798	0.292	157.779	0.573	0.130	2.504	0.247	0.061	1.347
	std	0.161	0.274	0.207	5.684	0.126	0.013	2.504	0.247	0.061	1.347
				(1					
	Loc 1	1.661	0.274	0.110	156.475	0.106	0.095	3.715	0.166	0.020	1.164
Sept-12	Loc 2	1.824	0.368	0.079	188.520	0.108	0.109	2.079	0.174	0.008	0.421
	Loc 3	0.624	0.019	0.085	437.629	0.383	0.022	3.715	0.127	0.019	0.101
	Sum	4.109	0.661	0.274	782.624	0.597	0.226	9.509	0.467	0.047	1.686
	mean	1.370	0.220	0.091	260.875	0.199	0.075	3.170	0.156	0.016	0.562
	std	0.651	0.181	0.061	153.910	0.159	0.027	0.945	0.025	0.007	0.545
	Loc 1	1.028	0.323	0.268	167.239	0.207	0.129	4.832	0.010	0.012	0.735
0 1 10	Loc 2	1.215	0.412	0.187	152.642	0.209	0.068	2.138	0.012	0.028	3.854
Octo-12	Loc 3	0.351	0.035	0.201	172.681	0.212	0.379	2.460	0.152	0.012	1.557
	Sum	2.594	0.770	0.665	492.562	0.628	0.576	9.430	0.174	0.052	6.146
	mean	0.865	0.257	0.218	164.187	0.209	0.192	3.143	0.058	0.017	2.049
	std	0.455	0.197	0.043	10.362	0.003	0.065	1.471	0.081	0.009	1.617
	Loc 1	0.804	0.480	0.157	163.885	0.145	0.302	4.292	0.045	0.043	1.032
	Loc 2	0.764	0.394	0.099	200.041	0.212	0.215	4.965	0.032	0.022	2.219
Nov 12	Loc 3	0.762	0.492	0.053	277.330	0.388	0.277	2.036	0.024	0.016	0.840
Nov-12	Sum	2.330	1.294	0.309	641.256	0.745	0.794	11.293	0.101	0.081	4.091
	mean	0.777	0.431	0.103	213.752	0.248	0.265	3.764	0.034	0.027	1.364
	std	0.024	0.053	0.052	57.952	0.126	0.045	1.534	0.011	0.014	0.747

		Sum of	Df	Mean Square	F	Sig
		Square				
	Between Groups	2.170	2	1.085	4.40	0.036
Al	Within groups	1.619	6	2.698	2	
	Total	3.789	8			
	Between Groups	181.934	2	90.967	16.2	0.004
Cr	Within groups	33.504	6	8.257	91	
	Total	215.438	8	5		
	Between Groups	17.549	2	8.775	0.07	0.932
Mn	Within groups	737.095	6	2.239	1	
	Total	754.645	8			
	Between Groups	335109.021	2	167550.511	2.26	0.027
Fe	Within groups	3.838E6	6	639693.961	2	
	Total	4.173E6	8			
	Between Groups	34.311	2	17.155	2.09	0.033
Ni	Within groups	35.476	6	5.913	1	
	Total	69.787	8			
	Between Groups	1.317	2	1.659	2.55	0.025
Cu	Within groups	1.546	6	0.741	6	
	Total	2.863	8			
	Between Groups	121.216	2	60.608	4.14	0.017
Zn	Within groups	87.789	6	14.631	2	
	Total	209.005	8			
	Between Groups	0.127	2	0.063	0.05	0.950
As	Within groups	7.426	6	1.238	1	
	Total	7.553	8			
	Between Groups	2.402	2	5.201	1.01	0.006
Cd	Within groups	1.185	6	1.280	7	
	Total	3.587	8			
	Between Groups	76.442	2	38.221	1.35	0.003
Pb	Within groups	169.443	6	28.240	3	
	Total	245.885	8			
<u> </u>	·					-

ONE-WAY ANOVA of heavy metals concentrations in sediment of three sampling Balok River

		Sum of	df	Mean	F	Sig
		Square		Square		
	Between Groups	1.528E8	2	15.483	14.890	0.005
Al	Within groups	3.078E7	6			
	Total	1.836E8	8			
	Between Groups	30.965	2	15. <mark>48</mark> 3	0.618	0.570
Cr	Within groups	150.214	6	1		
	Total	181.180	8			
	Between Groups	624.820	2	312.410	14.438	0.005
Mn	Within groups	129.825	6			
	Total	754.645	8			
	Between Groups	3.418E7	2	1.709E7	13.577	0.006
Fe	Within groups	7552403.55	6			
	Total	4.173E7	8			
	Between Groups	28.124	2	14.062	2.025	0.213
Ni	Within groups	41.663	6			
	Total	69.787	8			
	Between Groups	0.169	2	0.085	0.188	0.833
Cu	Within groups	2.694	6			
	Total	2.863	8			
	Between Groups	48.696	2	24.348	0.911	0.451
Zn	Within groups	160.309	6		£	
	Total	209.005	8			
	Between Groups	7.076	2	3.538	44.507	0.000
As	Within groups	0.477	6			
	Total	7.553	8			
	Between Groups	0.332	2	0.166	0.794	0.494
Cd	Within groups	1.255	6			
	Total	1.587	8			
	Between Groups	96.610	2	48.305	1.942	0.224
Pb	Within groups	149.275	6			
	Total	245.885	8			

ONE-WAY ANOVA of heavy metals concentrations in sediment Balok River during November 2010 until July 2011

		Sum of	df	Mean	F	Sig
		Square		Square		
	Between Groups	3.443	2	1.721	0.578	0.0053
Al	Within groups	17.854	6			
	Total	21.297	8			
	Between Groups	0.074	2	0.037	1.848	0.237
Cr	Within groups	0.121	6	5		
	Total	0.195	8			
	Between Groups	0.007	2	0.003	0440	0.663
Mn	Within groups	0.047	6			
	Total	0.053	8			
	Between Groups	0.001	2	0.001	3.347	0.106
Ni	Within groups	0.001	6			
	Total	0.002	8			
	Between Groups	0.016	2	0.005	1.487	0.002
Cu	Within groups	0.029	6			
	Total	0.045	8			
	Between Groups	46.741	2	3.370	1.944	0.000
Zn	Within groups	10.400	6			
	Total	57.141	8			
	Between Groups	0.008	2	0.004	0.197	0.826
As	Within groups	0.115	6			
	Total	0.123	8	- I		
	Between Groups	0.012	2	0.006	0.792	0.495
Cd	Within groups	0.046	6			
	Total	0.058	8			
	Between Groups	0.006	2	0.003	0.195	0.828
Pb	Within groups	0.100	6			
	Total	0.106	8			

ONE-WAY ANOVA of heavy metals concentrations in water Balok River for three sampling points

		Sum of	df	Mean	F	Sig
		Square		Square		
	Between Groups	13.786	2	6.893	5.506	0.044
Al	Within groups	7.511	6			
	Total	21.297	8			
	Between Groups	0.066	2	0.033	1.539	0.289
Cr	Within groups	0.129	6	-		
	Total	0.195	8			
	Between Groups	0.026	2	0.013	2.883	0.133
Mn	Within groups	0.027	6			
	Total	0.053	8			
	Between Groups	5419.070	2	2709.535	0.299	0.752
Fe	Within groups	54434.203	6			
	Total	59853.273	8			
	Between Groups	0.000	2	0.000	0.585	0.586
Ni	Within groups	0.002	6			
	Total	0.002	8			
	Between Groups	0.005	2	0.003	0.661	0.550
Cu	Within groups	0.024	6			
	Total	0.029	8			
	Between Groups	5.479	2	2.739	1.528	0.029
Zn	Within groups	10.759	6			
	Total	16.238	8			
	Between Groups	0.108	2	0.054	22.329	0.002
As	Within groups	0.015	6			
	Total	0.123	8			
	Between Groups	0.023	2	0.011	1.962	0.221
Cd	Within groups	0.035	6			
	Total	0.058	8			
	Between Groups	0.077	2	0.038	7.859	0.021
Pb	Within groups	0.029	6			
	Total	0.106	8			
		-	•			

ONE-WAY ANOVA of heavy metals concentrations in water Balok River during November 2010 until July 2011

The average of heavy metals concentrations in sediment Tunggak River (ppm) of three sampling points

AVERAGE OF HEAVY METALS CONCENTRATION IN SEDIMENT OF THREE SAMPLING POINT TUNGGAK RIVER											
Location	Month	Al	Cr	Mn	Fe	Ni	Cu	Zn	As	Cd	Pb
	Nov-10	5789.053	5.740	29.280	4689.890	2.503	2.510	19.703	1.963	0.024	4.590
Location 1	Mar-11	7781.000	6.192	43.686	5 537.461	2.934	2.340	24.191	3.054	0.152	7.482
	Jul-11	6806.137	7.778	52.735	5083.174	3.111	3.038	35.288	2.483	0.227	7.080
	sum	20376.190	19.710	125.700	15310.525	8.548	7.888	79.182	7.501	0.403	19.151
	mean	6792.063	6.570	41.906	5103.508	2.849	2.629	26.394	2.500	0.134	6.384
	std	996.048	1.070	11.829	424.151	0.313	0.364	8.022	0.546	0.103	1.567
	Nov-10	12964.830	10.260	39.370	5813.160	5.890	2.530	26.327	0.923	0.133	2.170
Location 2	Mar-11	9858.034	10.431	47.511	6009.463	4.093	3.923	33.122	1.904	0.148	5.112
	Jul-11	13805.034	9.363	45.765	7339.536	8.123	4.167	42.231	2.655	0.168	6.467
	sum	36627.898	30.054	132.645	19162.159	18.106	10.620	101.680	5.483	0.449	13.749
	mean	12209.299	10.018	44.215	6387.386	6.035	3.540	33.893	1.828	0.150	4.583
	std	2079.140	0.574	4.286	830.407	2.019	0.883	7.980	0.868	0.018	2.197
				P S							
	Nov-10	8865.53	11.14	64.050	7151.607	3.610	6.450	63.740	1.373	0.110	10.546
Location 3	Mar-11	9664.032333	11.5317	55.661	7078.460	7.514	5.962	73.764	1.451	0.153	4.823
	Jul-11	11211.099	12.4273	67.737	6864.570	9.689	8.214	79.753	1.981	0.181	7.406
	sum	29740.661	35.099	187.448	21094.637	20.814	20.626	217.257	4.805	0.444	22.775
	mean	9913.554	11.700	62.483	7031.546	6.938	6.875	72.419	1.602	0.148	7.592
	std	1192.526	0.660	6.189	149.158	3.080	1.185	8.091	0.331	0.036	2.866

The average of heavy metals concentrations in sediment Tunggak River (ppm) during November 2010 until July 2011

AVERAGE OF HEAVY METALS CONCENTRATION IN SEDIMENT DURING NOVEMBER 2010 UNTIL JULY 2011									2011		
Month	Location	Al	Cr	Mn	Fe	Ni	Cu	Zn	As	Cd	Pb
	Loc 1	5789.053	5.740	29.280	4689.890	2.503	2.510	19.703	1.963	0.024	4.590
Nov-10	Loc 2	12964.830	10.260	39.370	5813.160	5.890	2.530	26.327	0.923	0.133	2.170
	Loc 3	8865.530	11.140	64.050	7151.607	3.610	6.450	63.740	1.373	0.110	10.546
	Sum	27619.413	27.140	132.700	17654.657	12.003	11.490	109.770	4.260	0.267	17.306
	mean	9206.471	9.047	44.233	5884.886	4.001	3.830	36.590	1.420	0.089	5.769
	std	3600.017	2.897	17.888	1232.425	1.727	2.269	23.745	0.522	0.058	4.311
	Loc 1	7781.000	6.192	43.686	5537.461	2.934	2.340	24.191	3.054	0.152	7.482
Mar-11	Loc 2	9858.034	10.431	47.511	6009.463	4.093	3.923	33.122	1.904	0.148	5.112
	Loc 3	9664.032	11.532	55.661	7078.460	7.514	5.962	73.764	1.451	0.153	4.823
	Sum	27303.066	28.155	146.857	18625.384	14.541	12.225	131.078	6.409	0.453	17.416
	mean	9101.022	9.385	48.952	6208.461	4.847	4.075	43.693	2.136	0.151	5.805
	std	1147.263	2.819	6.116	789.538	2.381	1.816	26.423	0.826	0.003	1.459
		Al	Cr	Mn	Fe	Ni	Cu	Zn	As	Cd	Pb
	Loc 1	6806.137	7.778	52.735	5083.174	3.111	3.038	35.288	2.483	0.227	7.080
Jul-11	Loc 2	13805.034	9.363	45.765	7339.536	8.123	4.167	42.231	2.655	0.168	6.467
	Loc 3	11211.099	12.427	67.737	6864.570	9.689	8.214	79.753	1.981	0.227	7.406
	Sum	31822.270	29.568	166.237	19287.280	20.923	15.419	157.271	7.119	0.622	20.952
	mean	10607.423	9.856	55.412	6429.093	6.974	5.140	52.424	2.373	0.207	6.984
	std	3538.285	2.364	11.228	1189.547	3.436	2.722	23.921	0.350	0.034	0.477

AVERAGE OF HEAVY METALS CONCENTRATION IN WATER OF THREE SAMPLING POINT TUNGGAK RIVER											
Location	Month	Al	Cr	Mn	Fe	Ni	Cu	Zn	As	Cd	Pb
	12-Nov-10	0.002	0.002	0.200	2.990	0.010	0.005	0.092	0.013	0.004	0.040
	20-Mar-11	1.073	0.247	0.363	4.373	0.044	0.176	0.094	0.281	0.152	0.073
	13-Jul-11	0.759	0.002	0.044	3.443	0.043	0.064	0.077	0.014	0.042	0.059
Location 1	11-Jul-12	0.238	0.429	0.535	2.197	0.108	0.083	0.085	0.236	0.061	0.182
	20-Sept-12	0.364	0.176	0.712	5.027	0.076	0.117	0.162	0.183	0.114	0.277
	08-Oct-12	1.092	1.235	0.890	4.045	0.015	0.051	1.731	0.239	0.034	1.264
	06-Nov-12	0.627	0.119	0.295	1.964	0.187	0.062	0.082	0.116	0.028	1.875
	Sum	4.155	2.210	3.040	24.040	0.482	0.559	2.321	1.082	0.435	3.770
	mean	0.594	0.318	0.434	3.434	0.069	0.084	0.332	0.155	0.062	0.539
	std	0.120	0.042	0.113	1.960	0.018	0.023	0.070	0.034	0.031	0.126
	12-Nov-10	0.004	0.004	0.350	7.810	0.012	0.002	0.130	0.010	0.002	0.043
	20-Mar-11	0.584	4.783	0.334	7.703	0.044	0.174	3.462	0.253	0.011	0.124
	13-Jul-11	0.396	2.359	0.114	6.550	0.009	0.138	1.353	0.147	0.005	0.212
Location 2	11-Jul-12	0.852	0.128	0.872	4.122	0.192	0.066	1.128	0.421	0.002	0.159
	20-Sept-12	0.625	0.299	0.544	5.246	0.076	0.092	0.073	0.157	0.007	0.187
	08-Oct-12	1.256	1.611	0.299	4.119	0.087	0.079	0.271	0.078	0.018	0.663
-	06-Nov-12	0.659	0.783	0.214	3.202	0.207	0.015	0.411	0.389	0.009	1.031
	Sum	4.376	9.967	2.278	38.752	0.447	0.566	6.828	1.455	0.054	2.400
	mean	0.625	1.424	0.390	5.536	0.064	0.105	0.975	0.222	0.008	0.343
	std	0.218	0.390	0.102	3.916	0.019	0.047	0.086	0.017	0.003	0.094

The average of heavy metals concentrations in water Tunggak River (ppm) of three sampling points

	12-Nov-10	0.007	0.003	0.302	3.400	0.021	0.020	0.166	0.008	0.001	0.045
	20-Mar-11	1.823	0.204	0.427	16.702	0.045	0.171	1.984	0.209	0.124	0.152
	13-Jul-11	0.720	0.032	0.501	13.267	0.051	0.157	0.175	0.125	0.067	0.178
Location 3	11-Jul-12	0.014	0.008	0.432	10.673	0.011	0.068	0.112	0.765	0.046	0.291
Location 5	20-Sept-12	2.006	0.107	1.328	8.519	0.067	0.044	2.782	0.311	0.008	0.377
	08-Oct-12	0.407	0.405	0.771	4.412	0.102	0.019	2.508	0.028	0.053	1.225
	06-Nov-12	1.981	0.001	0.619	8.331	0.084	0.239	1.116	0.493	0.119	2.348
	Sum	6.958	0.760	4.381	65.304	0.381	1.866	8.842	1.939	0.419	4.616
	mean	1.021	0.109	0.626	9.329	0.070	0.267	1.263	0.291	0.064	0.659
	std	0.588	0.019	0.296	2.114	0.016	0.053	0.147	0.053	0.012	0.033

UMP

The average of heavy metals concentrations in water Tunggak River (ppm) during November 2010 until November 2012

AVERA	AVERAGE OF HEAVY METALS CONCENTRATION IN WATER TUNGGAK DURING NOV 2010 UNTIL NOV 2012										
Month	Location	Al	Cr	Mn	Fe	Ni	Cu	Zn	As	Cd	Pb
	Loc 1	0.002	0.002	0.200	2.990	0.010	0.005	0.092	0.013	0.004	0.040
Nov-10	Loc 2	0.004	0.004	0.350	7.810	0.012	0.002	0.130	0.010	0.002	0.043
	Loc 3	0.007	0.003	0.302	3.400	0.021	0.020	0.166	0.008	0.001	0.045
	Sum	0.013	0.009	0.853	14.200	0.043	0.027	0.387	0.032	0.007	0.128
	mean	0.004	0.003	0.284	4.733	0.014	0.009	0.129	0.011	0.003	0.043
	std	0.002	0.001	0.077	2.672	0.006	0.010	0.037	0.003	0.002	0.002
	Loc 1	1.073	0.247	0.363	4.373	0.0440	0.176	0.094	0.281	0.152	0.073
Mar-11	Loc 2	0.584	4.783	0.334	7.703	0.0437	0.174	3.462	0.253	0.011	0.124
	Loc 3	1.823	0.204	0.427	16.702	0.0447	0.171	1.984	0.209	0.124	0.152
	Sum	3.480	5.235	1.125	28.778	0.132	0.522	5.540	0.743	0.288	0.348
	mean	1.160	1.745	0.375	9.593	0.044	0.174	1.847	0.248	0.096	0.116
	std	0.624	0.631	0.047	6.378	0.001	0.003	1.608	0.036	0.075	0.040
	Loc 1	0.759	0.002	0.044	3.443	0.043	0.064	0.077	0.014	0.042	0.059
Jul-11	Loc 2	0.396	2.359	0.114	6.550	0.009	0.138	1.353	0.147	0.005	0.212
	Loc 3	0.720	0.032	0.501	13.267	0.051	0.157	0.175	0.125	0.067	0.178
	Sum	1.875	2.392	0.660	23.260	0.103	0.359	1.605	0.286	0.114	0.449
	mean	0.625	0.797	0.220	7.753	0.034	0.120	0.535	0.095	0.038	0.150
	std	0.199	0.352	0.146	5.021	0.022	0.049	0.210	0.071	0.032	0.080

Month	Location	Al	Cr	Mn	Fe	Ni	Cu	Zn	As	Cd	Pb
	Loc 1	0.238	0.429	0.535	2.197	0.108	0.083	0.085	0.236	0.061	0.182
July-12	Loc 2	0.852	0.128	0.872	4.122	0.192	0.066	1.128	0.421	0.002	0.159
5	Loc 3	0.014	0.008	0.432	10.673	0.011	0.068	0.112	0.765	0.046	0.291
	Sum	1.104	0.565	1.839	16.992	0.311	0.217	1.323	1.422	0.109	0.632
	mean	0.368	0.188	0.613	5.664	0.104	0.072	0.441	0.474	0.036	0.211
	std	0.434	0.217	0.230	4.443	0.091	0.009	0.595	0.268	0.031	0.071
	Loc 1	0.364	0.176	0.712	5.027	0.076	0.117	0.162	0.183	0.114	0.277
Sep-12	Loc 2	0.625	0.299	0.544	5.246	0.076	0.092	0.073	0.157	0.007	0.187
	Loc 3	2.006	0.107	1.328	8.519	0.067	0.044	2.782	0.311	0.008	0.377
	Sum	2.995	0.582	2.584	18.792	0.219	0.253	3.017	0.651	0.129	0.841
	mean	0.998	0.194	0.861	6.264	0.073	0.084	1.006	0.217	0.043	0.280
	std	0.882	0.097	0.413	1.956	0.005	0.037	1.539	0.082	0.061	0.095
	Loc 1	1.092	1.235	0.890	4.045	0.015	0.051	1.731	0.239	0.034	1.264
	Loc 2	1.256	1.611	0.299	4.119	0.087	0.079	0.271	0.078	0.018	0.663
Oct-12	Loc 3	0.407	0.405	0.771	4.412	0.102	0.019	2.508	0.028	0.053	1.225
	Sum	2.775	3.251	1.960	12.576	0.204	0.149	4.5100	0.345	0.105	3.152
	mean	0.918	1.084	0.653	4.192	0.068	0.050	1.503	0.115	0.035	1.051
	std	0.450	0.617	0.313	0.194	0.047	0.030	1.136	0.110	0.018	0.336

		Sum of	df	Mean	F	Sig
		Square		Square		
	Between Groups	4.808E7	2	2.404E7	10.507	0.011
Al	Within groups	1.373E7	6			
	Total	6.180E7	8			
	Between Groups 🥔	41.030	2	20.515	32.221	0.001
Cr	Within groups	3.820	6	5		
	Total	44.8 <mark>50</mark>	8			
	Between Groups	762.412	2	381.206	5.816	0.039
Mn	Within groups	393.256	6			
	Total	1155.668	8			
	Between Groups	5785708.926	2	2892854.4	9.730	0.013
Fe	Within groups	1783961.473	6	63		
	Total	7569670.400	8			
	Between Groups	27.679	2	13.840	3.039	0.123
Ni	Within groups	27.323	6			
	Total	55.002	8			
	Between Groups	29.993	2	14.996	19.418	0.002
Cu	Within groups	4.634	6			
	Total	34.626	8			
	Between Groups	3658.768	2	1829.384	28.362	0.001
Zn	Within groups	387.009	6			
	Total	4045.776	8			
	Between Groups	1.310	2	0.655	1.692	0.261
As	Within groups	2.323	6			
	Total	3.634	8	1		
	Between Groups	0.001	2	0.000	0.054	0.948
Cd	Within groups	0.024	6			
	Total	0.025	8			
	Between Groups	13.754	2	6.877	1.332	0.332
Pb	Within groups	30.988	6			
	Total	44.743	8			

ONE-WAY ANOVA of heavy metals concentrations in sediment Tunggak River for three sampling points

		Sum of	df		Mean Square	F	Sig
		Square					
	Between Groups	3098936.443	2		1549468.222	0.158	0.857
Al	Within groups	5.870E7	6				
	Total	6.180E7	8				
	Between Groups	0.991	2		0.496	0.068	0.935
Cr	Within groups	43.858	6				
	Total	44.850	8		1		
Mn	Between Groups	188. <mark>949</mark>	2		94.474	0.586	0.585
IVIII	Within groups	966.720	6				
	Total	1155.668	8				
	Between Groups	447749.042	2		223874.521	0.189	0.833
Fe	Within groups	7121921.358	6				
	Total	7569670.400	8				
	Between Groups	14.082	2		1.455	0.275	0.768
Ni	Within groups	40.920	6				
	Total	55.002	8				
	Between Groups	2.910	2		7.041	1.032	0.412
Cu	Within groups	31.716	6				
	Total	34.626	8				
	Between Groups	377.401	2		188.700	0.309	0.745
Zn	Within groups	3668.376	6				
	Total	4045.776	8				
	Between Groups	1.478	2		0.739	2.058	0.209
As	Within groups	2.155	6				
	Total	3.634	8				
~ .	Between Groups	0.016	2		0.008	5.735	0.041
Cd	Within groups	0.008	6				
	Total	0.025	8	-			
	Between Groups	2.868	2		1.434	0.206	0.820
Pb	Within groups	41.874	6				
	Total	44.743	8				

ONE-WAY ANOVA of heavy metals concentrations in sediment Tunggak River during November 2010 until July 2011

		Sum of	df	Mean	F	Sig
		Square		Square		
	Between Groups	0.410	2	0.205	0.500	0.630
Al	Within groups	2.457	6			
	Total	2.867	8			
	Between Groups	10.583	2	5.291	2.765	0.141
Cr	Within groups	11.484	6			
	Total	22.066	8			
	Between Groups	0.068	2	0.034	1.913	0.228
Mn	Within groups	0.106	6			
	Total	0.174	8			
	Between Groups	84.848	2	42.424	2.615	0.153
Fe	Within groups	97.337	6			
	Total	182.185	8			
	Between Groups	0.000	2	0.000	0.686	0.539
Ni	Within groups	0.002	6			
	Total	0.002	8			
	Between Groups	0.002	2	0.001	0.121	0.888
Cu	Within groups	0.045	6			
	Total	0.047	8			
	Between Groups	3.671	2	1.835	1.398	0.317
Zn	Within groups	7.875	6			
	Total	11.545	8		1	
	Between Groups	0.002	2	0.001	0.055	0.947
As	Within groups	0.098	6			
	Total	0.100	8			
	Between Groups	0.007	2	0.003	1.076	0.399
Cd	Within groups	0.019	6	1		
	Total	0.026	8			
	Between Groups	0.016	2	0.008	3.195	0.114
Pb	Within groups	0.150	6			
	Total	0.031	8			

ONE-WAY ANOVA of heavy metals concentrations in water Tunggak River for three sampling points

		Sum of	df	Mean Square	F	Sig
		Square				
	Between Groups	2.007	2	1.004	7.015	0.027
Al	Within groups	0.858	6			
	Total	2.865	8			
	Between Groups	4.562	2	2. <mark>2</mark> 81	0.782	0.490
Cr	Within groups	17.505	6	-		
	Total	22.067	8			
	Between Groups	0.037	2	0.018	0.798	0.493
Mn	Within groups	0.137	6			
	Total	0.174	8			
	Between Groups	36.117	2	18.058	0.742	0.515
Fe	Within groups	146.069	6			
	Total	182.185	8			
	Between Groups	0.001	2	0.001	3.903	0.082
Ni	Within groups	0.001	6			
	Total	0.002	8			
	Between Groups	0.042	2	0.021	25.229	0.001
Cu	Within groups	0.005	6			
	Total	0.047	8			
	Between Groups	4.834	2	2.417	2.161	0.196
Zn	Within groups	6.711	6			
	Total	11.545	8			
	Between Groups	0.087	2	0.043	20.315	0.002
As	Within groups	0.013	6			
	Total	0.100	8			
	Between Groups	0.013	2	0.007	3.049	0.122
Cd	Within groups	0.013	6	A		
	Total	0.026	8			
	Between Groups	0.008	2	0.004	1.138	0.381
Pb	Within groups	0.022	6			
	Total	0.031	8			

ONE-WAY ANOVA of heavy metals concentrations in water Tunggak River during November 2010 until July 2011

		(11444)	x0)				
Deremetere	(I Inita)			Class	ses		
Parameters	(Units)	I	IIA	IIB	III	IV	V
Ammonical Nitrogen	mg/l	0.1	0.3	0.3	0.9	2.7	> 2
BOD	mg/l	1	3	3	6	12	> 12
COD	mg/l	10	25	25	50	100	> 100
DO	mg/l	7	5 - 7	5 - 7	3 - 5	< 3	< 1
pН	6	6.5- <mark>8.5</mark>	6.5 - 9.5	6 - 9	5 - 9	5 - 9	
Colour	TCU	15	150	150			
Electrical Conductivity	mmhos/cm	1000	1000		-	6000	-
Floatables	-	Ν	Ν	Ν	-	-	-
Odour	-	Ν	Ν	Ν	-	-	-
Salinity	°/ _{oo}	0.5	1	-	-	-	-
Taste	-	Ν	Ν	Ν	-	-	-
Total Dissolved Solids	mg/l	500	1000	-	-	-	-
Total Suspended Solids	mg/l	25	50	50	150	300	> 300
Temperature	°C	-	Normal +2	-	Normal +2	-	-
Turbidity	NTU	5	50	50	7 -	-	-
Faecal Caliform*	counts/100ml	10	100	400	5000 (2000)@	5000 (2000)	-
Total Coliform	counts/100ml	100	5000	50000	50000	50000	>50000

NTERIM NATIONAL WATER QUALITY STANDARDS FOR MALAYSIA (INWQS)

Note:-	NUMP
N	No visible floatable materials/debris
	or No objectionable odour
	or No objectionable taste

* Geometric Mean

@ Maximum not to be exceeded

-	<i></i>			Classes		
Parameters	s (Units)	I	IIA / IIB	III [@]	IV	v
A1	mg/l		-	(0.06)	0.5	
As	mg/l	-	0.05	0.4 (0.05)	0.1	
Ba	mg/l	~	1		-	
Cd	mg/l	N	0.01	0.01* (0.001)	0.01	L
Cr(Vl)	mg/l	А	0.01	1.4 (0.05)	0.1	E
Cr(lll)	mg/l		0.05	2.5	-	V
Cu	mg/l	Т	1	-	0.2	Е
Hardness	mg/l	U	250	-	-	L
Ca	mg/l	R	-	-	-	S
Mg	mg/l	А	-	/	-	
Na	mg/l	L			3 SAR	А
К	mg/l		M	D /	-	В
Fe	mg/l	~	0.3	1	1 (leaf)	0
					5 (others)	V
Pb	mg/l		0.05	0.02* (0.01)	5	Е
Mn	mg/l		0.1	0.2	0.2	
Hg	mg/l		0.001	0.004 (0.0001)	0.002	IV
Ni	mg/l	L	0.05	0.9*	0.2	
Se	mg/l	Е	0.01	0.25	0.02	
Ag	mg/l		0.05	0.0002	-	

INTERIM NATIONAL WATER QUALITY STANDARDS FOR MALAYSIA (INWQS) (continued)

Sn	mg/l	V	-	0.004	-
U	mg/l	v	-	-	-
Zn	mg/l	E	5	0.4*	2
В	mg/l	L	1	(3.4)	0.8
Cl	mg/l		200	-	80
Cl ₂	mg/l		-	(0.02)	-
CN	mg/l	~	0.02	0.06 (0.02)	
F	mg/l		1.5	10	1
NO ₂	mg/l		0.4	0.4 (0.03)	-
NO ₃	mg/l		7	-	5
Р	mg/l		0.2	0.1	-
Si	mg/l		50	-	-
SO_4	mg/l		250	-	-
S	mg/l		0.05	(0.001)	-
CO ₂	mg/l				-
Gross-a	Bq/l		0.1		-
Gross-b	Bq/l	U	1	- A	-
Ra-266	Bq/l		< 0.1	<u> </u>	-
Sr-90	Bq/l		< 1	-	-
<u> </u>	Note:-				

@

Maximum (unbracketed) and 24-hour average (bracketed) concentrations

Parameters		(11		Classes						
		(Units)	1	IIA / IIB	III [@]	IV	v			
CCE		m g/l		500	-	-	L			
MBA/BAS		m g/l	N A T	500	5000 (200)	-	E V E			
O&G (mineral)		m g/l	U R A	40;N	Ν	-	L S			
O&G (emulsified / edi	ble)	m g/l	L	7000;N	Ν	-	A B O			
РСВ		m g/l	L E	0.1	6 (0.05)	-	V E			
Phenol		m g/l	V E	10	-	-	IV			
Aldrin/Dieldrin		m g/l	L S	0.02	0.2 (0.01)	-				
ВНС		m g/l		2	9 (0.1)	-				
Chlordane		m g/l		0.08	2 (0.02)	-				
t-DDT		m g/l		0.1	1 (0.01)	-				
Endosulfan		m g/l		10	-	-				
Heptachlor/Epoxide		m g/l	TV.	0.05	0.9 (0.06)	-				
Lindane		m g/l		2	3 (0.4)	-				
2,4-D		m g/l		70	450	-				
2,4,5-T		m g/l		10	160	-				
2,4,5-TP		m g/l		4	850	-				
Paraquat		m g/l		10	1800	-				

INTERIM NATIONAL WATER QUALITY STANDARDS FOR MALAYSIA (INWQS) (continued)

Note:-

Ν

Free from visible film, sheen, discoloration and deposits

@ Maximum (unbracketed) and 24-hr average (bracketed) concentrations

Class	<u>s</u>	Uses						
1		Conservation of natural environment						
		Water supply l - practically no treatment necessary (except by disinfection of boiling only)						
		Fishery 1 - very sensitive aquatic species						
llA		Water supply ll - conventional treatment required						
		Fishery II sensitive aquatic species						
llB		Recreational use with body contact						
Ш		Water supply III - extensive treatment required						
		Fishery III - common, of economic value and tolerant species						
187		Inviantion						
ĨV		Infigation						
V		None of the above						

			CLASSES					
PARAME'	TERS	UNIT	I	IIA / IIB	III#	IV	V	
Al		mg/l		-	- (0.06)	0.5		
As		mg/l		0.05	0.4 (0.05)	0.1		
Ba		mg/l		1	-	-		
Cd		mg/l		0.01	0.01* (0.001)	0.01		
Cr (IV)		mg/l		0.05	1.4 (0.05)	0.1		
Cr (III)		mg/l			2.5	-		
Cu		mg/l	1 mar 1	0.02	-	0.2		
Hardness		mg/l		250	-	-		
Ca		mg/l	Ν	-	-	-	L	
Mg		mg/l	А	-	-	-	Е	
Na		mg/l	Т	-	-	3 SAR	V	
K		mg/l	U	-	-	-	Е	
Fe		mg/l	R	1	1	1 (Leaf) 5(Others)	L	
Pb		mg/l	А	0.05	0.02* (0.01)	5	S	
Mn		mg/l	L	0.1	0.1	0.2		
Hg		mg/l		0.001	0.004 (0.0001)	0.002	А	
Ni		mg/l	L	0.05	0.9*	0.2	В	
Se		mg/l	Е	0.01	0.25 (0.04)	0.02	Ο	
Ag		mg/l	V	0.05	0.0002	-	V	
Sn		mg/l	Е	-	0.004	-	Е	
U		mg/l	L	-	-	-		
Zn		mg/l	S	5	0.4 *	2	IV	
В		mg/l		1	- (3.4)	0.8		
Cl		mg/l		200	-	80	•	
Cl_2		mg/l			- (0.02)	-		
CN		mg/l		0.02	0.06 (0.02)	-		
F		mg/l		1.5	10	1		
NO ₂		mg/l		0.4	0.4 (0.03)	-		
NO ₃		mg/l		7	-	5		
Р		mg/l		0.2	0.1	-		
Silica		mg/l		50	-	-		
SO_4		mg/l		250	-	-		
S		mg/l		0.05	- (0.001)	-		

INTERIM NATIONAL WATER QUALITY STANDARDS FOR MALAYSIA

CO ₂		mg/l			-	-	
Gross - alfa		Bq/L		0.1	-	-	
Gross - beta		Bq/L		1	-	-	
Ra - 226		Bq/L		< 0.1	-	-	
Sr - 90		Bq/L		<1	-	-	
CCE		ug/l		500	-	-	-
MBAS/BAS		ug/l		500	5000 (200)	-	-
O & G (Mine	ral)	ug/l		40 ; N	Ν	-	-
O & G (Emul edible)	sified	ug/l		7000 ; N	Ν	-	-
РСВ		ug/l		0.1	6 (0.05)	-	-
Phenol		ug/l		10	<u> </u>	-	-
Aldrin/Dieldr	in	ug/l	1 mar 1	0.02	0.2 (0.01)	-	-
BHC		ug/l		2	9 (0.1)	-	-
Chlordane		ug/l		0.08	2 (0.02)	-	-
t - DDT		ug/l	OR	0.1	(1)	-	-
Endosulfan		ug/l		10	-	-	-
Heptachlor / I	Epoxide	ug/l	А	0.05	0.9 (0.06)	-	-
Lindane		ug/l	В	2	3 (0.4)	-	-
2,4 -D		ug/l	S	70	450	-	-
2,4,5 - T		ug/l	Е	10	160	-	-
2,4, 5 - TP		ug/l	Ν	4	850	-	-
Paraquat		ug/l	Т	10	1800	-	-

* = At hardness 50 mg/l CaCO₃

= Maximum (unbracket) and 24 - hour average (bracketed) concentrations

N = Free from visible film sheen, discoloration and deposits

