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Environmental Impacts of Human Activities Monitored by PTEs Contamination of Stream Sediments along the Wad Malyan River

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Abstract:
Potentially toxic elements (PTEs) composition of the Wad Malyan stream sediments was examined using aqua regia extraction method. The concentration of major elements such as Na, Mg, Al, K, Ca, and Fe, is around background level, of which variation pattern from the upstream to the downstream does not show specific trends. Non-metal light elements, B, P, and S, and seven heavy metals, Cu, Cr, Ni, Zn, Ag, Au, and Hg, exhibit sudden increases at Ezzahra and its downstream, where populated and industrial zones are developed. The inflow of treated industrial wastewater is the possible source of the contamination. However other heavy metals such as Ba, Mo, Cd, Sb, Tl, Pb, and toxic metalloids As and Se show no significant increases of the concentration at Ezzahra and its downstream. The concentration of three PTEs, Hg, As, and Pb, exceeds the threshold values of environmental screening in the upstream area, from Jbal al Wost to Mohammediyya, which is probably due to illegally disposed solid wastes in the river.
Keywords:
Sediment contamination, Heavy metals, Treated wastewater, Solid waste disposal

I. Introduction

A reconnaissance survey of sediment quality along the Wad Malyan river was undertaken in response to concerns about the effects and extent of potentially toxic elements (PTEs) contamination from human activities such as agriculture, industry, urbanization, and effluents. In particular, the impacts of illegally disposed solid wastes in the river basin and the inflows of treated industrial/municipal wastewaters were examined.

II. Wad Malyan River and Sampling Sites

The Wad Malyan river flows from Sminja, 5 km west of Zaghwan, to Rades, industrial zone of Tunis urban zone, and into Mediterranean Sea. The total length of the river is about 60 km. Most of the river basin lies within the Tertiary to Quaternary sediments mainly composed of sand, silt and clay. The interval of upstream from Sminja to Al Khlidiyya lies on an agricultural zone (Plate 1), while the downstream is in populated area where various kinds of solid wastes are disposed in the river basin (Plates 2 to 4). In the downstream along populated area, treated industrial wastewater and treated municipal wastewater also flow into the river from wastewater treatment stations; Urban Wastewater Treatment Plant (Ben Arous), Industrial Wastewater Treatment Plant (Ben Arous), and Municipal Wastewater Stabilization Ponds (Rades) (plate 5).

A total of 12 stream sediment samples were collected for analyses. The location of sampling sites is shown in Figure 1 and the field photographs are shown in Plates 1 to 6. The site information is summarized in Table 1.

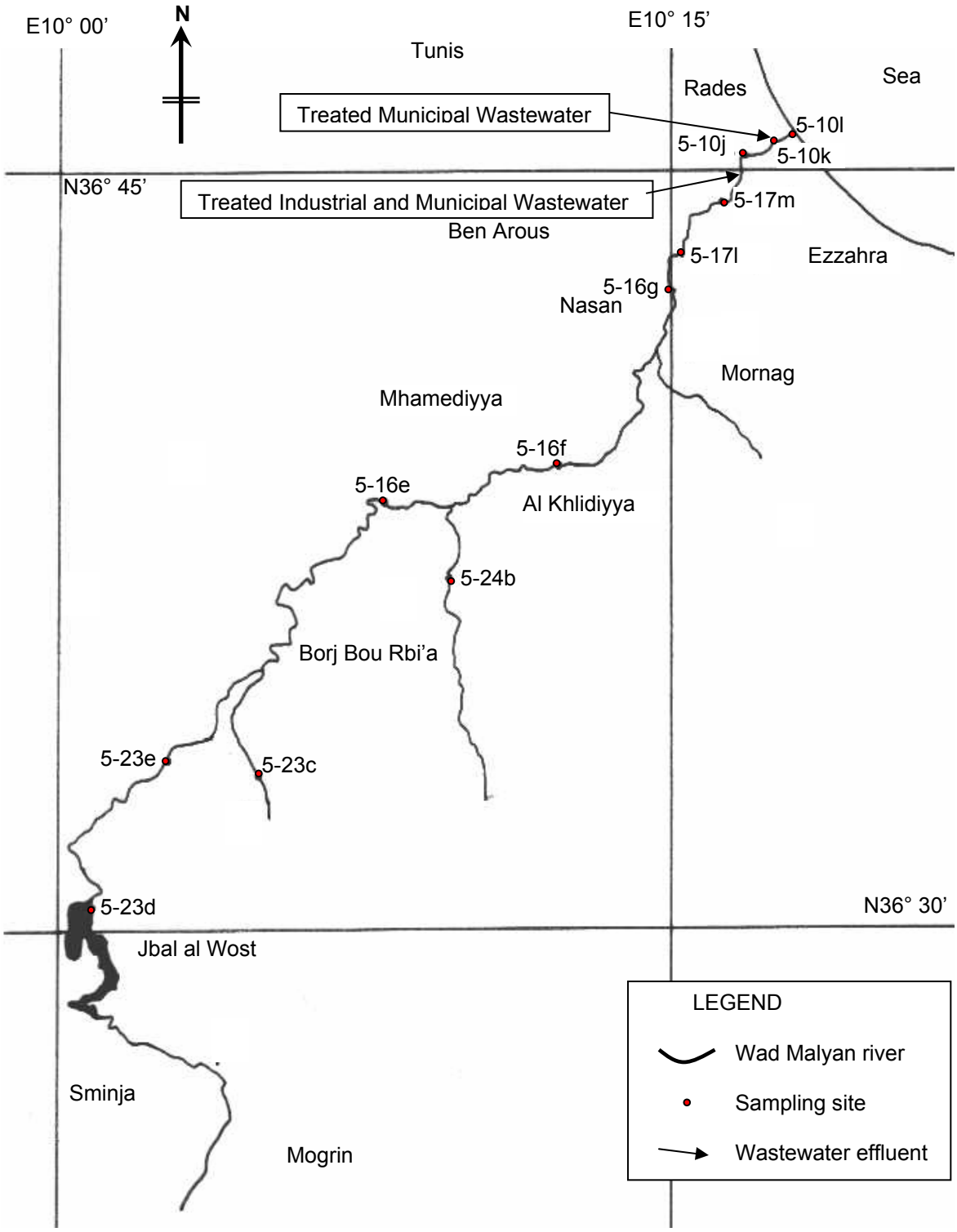

Figure 1: Location map for sampling site along the Wad Malyan river.

Plate1 (left): A view of the upper stream of the Wad Malyan river near Jbal al Wost.
Plate 2 (right): Illegally disposed solid wastes into Wad Malyan river near Nasan town

Plate3 (left): Illegally disposed solid wastes into the Wad Malyan near Mornag town
Plate 4 (right): The Wad Malyan river near Rades (Site 5-10j)

Plate 4 (right): Inflow of treated municipal wastewater into the Wad Malyan near Rades (Site 5-10k)
Plate 5 (right): Estuary of the Wad Malyan river (Site 5-10l)

Table 1: Summary of sampling sites

Site	Latitude	Longitude	Place/Description
5-23c	N36 33.02'	E10 04.84'	Jbal al Wost
5-23d	N36 30.60'	E10 00.62'	Jbal al Wost dam
5-23e	N36 33.56'	E10 02.46'	Jbal al Wost town
5-16e	N36 38.42'	E10 07.82'	Mohamediyya south, illegal solid wastes disposal
5-24b	N36 37.39'	E10 10.60'	Borj Bou Rbi'a
5-16f	N36 39.14'	E10 11.96'	Al Khlidiyya, illegal solid wastes disposal
5-16g	N36 42.61'	E10 14.95'	Nasan, illegal solid waste disposal
5-17l	N36 43.43'	E10 15.18'	Ben Arous east, illegal solid waste disposal
5-17m	N36 44.30'	E10 16.35'	Mornag road, illegal solid waste disposal
5-10j	N36 45.32'	E10 16.82'	Ezzahra, downstream of the inlet of treated industrial wastewater
5-10k	N36 45.53'	E10 17.48'	Rades, Inlet of treated municipal wastewater
5-10l	N36 45.81'	E10 17.90'	Rades, estuary

III. Analysis

The sediment samples collected were disintegrated and dried under room temperature, and powdered by a ceramic mill. In order to minimize the grain size effect, the powder samples were sieved by a 63 micron mesh and the finer fraction was used for the analysis (de Groot, 1995).

A 15.0 gm sample split was digested in 90 mL aqua regia (HCl-HNO_3-H_2O) at 95°C for one hour. The solution is diluted to 300 mL with distilled water. Analysis was made by an Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) and Mass Spectrometry (ICP-MS). Total 37 elements were measured: B, Na, Mg, Al, P, S, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, As, Se, Sr, Mo, Ag, Cd, Sb, Te, Ba, La, W, Au, Hg, Tl, Pb, Bi, Th, and U. The upper detection limit for Ag, Au, Hg, W, Se, Te, Tl, and Ga is 100 ppm, that for Mo, Co, Cd, Sb, Bi, Th, U, and B is 2 %, and that for Cu, Pb, Zn, Ni, Mn, As, V, La, and Cr is 10 %. The aqua regia digestion of sediment extracts only a fraction of the major elements (pseudo-total analysis) because silicates are not completely dissolved with this method. Owing to this limitation, results are total to near total for trace and base metals and possibly partial for rock-forming elements such as Na, Mg, Al, K, Ca, Mn, and Fe. However, environmentally concerned components like heavy metals or potentially toxic elements (PTEs; Alloway, 1995) not bound to silicates are efficiently dissolved (Ure, 1995), which is indicative for the assessment of toxicity.

IV. Results and Discussion

The result of chemical analysis using aqua regia extraction is shown in Table 2, and the concentration variation of individual elements is graphically displayed in Figures 2 to 4.

Table 2: Result of chemical analysis of the sediment samples

ELEMENT	B	Na	Mg	Al	P	S	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga
SAMPLES	ppm	%	%	%	%	%	%	%	ppm	%	ppm	ppm	ppm	%	ppm	ppm	ppm	ppm	ppm
Detection Limit	1	0.001	0.01	0.01	0.001	0.01	0.01	0.01	0.1	0.001	2	0.5	1	0.01	0.1	0.1	0.01	0.1	0.1
5-23c	8	0.724	0.62	1.07	0.029	0.39	0.10	15.07	3.6	< .001	24	24.2	471	3.99	21.9	35.1	25.86	98.1	3.0
5-23d	5	0.115	0.50	1.47	0.028	0.14	0.23	9.80	3.8	< .001	32	29.6	444	3.29	13.8	26.1	14.64	65.7	4.5
5-23e	6	0.094	0.46	1.12	0.036	0.05	0.14	12.05	3.3	< .001	23	24.5	375	2.77	14.0	25.1	24.32	90.4	3.2
5-16e	6	0.015	0.23	0.49	0.053	0.04	0.17	15.87	0.9	0.002	13	12.7	146	0.78	3.2	7.7	48.46	245.4	1.6
5-24b	4	0.014	0.13	0.32	0.063	0.09	0.11	9.68	0.7	0.003	10	9.2	102	0.47	2.7	6.3	13.47	72.6	1.1
5-16f	8	0.154	0.50	1.37	0.044	0.04	0.23	10.77	2.8	0.003	31	28.3	290	2.11	8.0	19.0	12.39	60.1	3.7
5-16g	9	0.114	0.46	1.22	0.118	0.09	0.22	13.26	3.0	< .001	29	30.0	288	1.93	7.7	18.5	19.12	113.2	3.7
5-17l	8	0.118	0.44	1.10	0.101	0.09	0.18	11.81	2.7	< .001	26	24.9	256	1.90	6.6	16.5	14.36	76.7	3.2
5-17m	6	0.049	0.46	1.14	0.074	0.04	0.22	12.16	2.5	< .001	31	28.1	315	1.98	7.8	18.4	14.45	85.6	3.3
5-10j	16	0.136	0.41	0.73	0.352	0.25	0.17	16.69	1.9	0.001	23	74.8	189	1.35	6.1	22.6	44.04	164.2	2.7
5-10k	3	0.046	0.10	0.16	0.095	0.23	0.03	7.41	0.9	0.001	10	30.0	121	0.66	2.7	9.3	15.59	61.8	0.5
5-10l	11	0.122	0.42	1.17	0.270	0.39	0.24	11.98	2.7	0.002	27	62.0	265	1.91	7.7	36.9	71.76	242.5	3.5

ELEMENT	As	Se	Sr	Mo	Ag	Cd	Sb	Te	Ba	La	W	Au	Hg	Tl	Pb	Bi	Th	U
SAMPLES	ppm	ppm	ppm	ppm	ppb	ppm	ppm	ppm	ppm	ppm	ppm	ppb	ppb	ppm	ppm	ppm	ppm	ppm
Detection Limit	0.1	0.1	0.5	0.01	2	0.01	0.02	0.02	0.5	0.5	0.2	0.2	5	0.02	0.01	0.02	0.1	0.1
5-23c	9.3	1.1	500.8	0.97	43	0.09	0.42	0.15	114.8	4.3	< .1	0.3	27	0.05	18.40	0.30	1.8	0.3
5-23d	35.4	0.6	240.0	0.72	49	0.11	0.36	0.09	79.4	4.9	< .1	0.2	28	0.08	15.51	0.19	2.3	0.4
5-23e	12.8	0.7	293.4	0.67	44	0.21	1.92	0.11	99.4	4.4	< .1	0.5	745	0.06	25.10	0.29	1.8	0.3
5-16e	16.3	0.5	255.1	0.60	71	0.63	4.68	0.08	160.6	4.0	< .1	0.9	649	0.05	237.50	0.07	0.8	0.3
5-24b	4.9	0.4	135.1	0.25	102	0.36	0.89	0.05	87.8	3.4	< .1	16.6	127	0.04	44.66	0.06	0.7	0.2
5-16f	5.8	0.5	315.7	0.45	47	0.17	0.19	0.07	133.8	7.3	< .1	1.5	62	0.07	14.67	0.11	2.7	0.5
5-16g	5.8	0.8	436.8	0.54	115	0.35	0.33	0.07	195.6	8.4	< .1	58.1	50	0.07	53.63	0.13	3.0	0.5
5-17l	5.3	0.8	457.3	0.47	71	0.22	0.56	0.07	179.4	7.2	< .1	12.8	53	0.05	49.28	0.12	2.8	0.4
5-17m	6.6	0.6	410.5	0.64	92	0.87	0.38	0.08	175.0	7.8	< .1	1.4	64	0.07	39.42	0.14	2.5	0.4
5-10j	10.0	1.2	573.6	1.01	1322	0.69	0.68	0.08	181.6	6.0	0.1	186.6	159	0.07	57.10	0.20	1.5	0.9
5-10k	7.7	0.6	290.6	0.82	519	0.17	0.30	0.04	39.9	3.0	< .1	75.4	35	0.02	15.80	0.07	0.3	0.3
5-10l	10.4	1.1	434.1	1.22	1336	0.79	0.59	0.07	222.3	7.7	< .1	206.1	226	0.10	77.39	0.33	2.3	0.8

The concentration of Ti and W is very low around the detection limit. Other elements show meaningful concentration for the interpretation. The concentration of major elements such as Na, Mg, Al, K, Ca, and Fe, is around background level, of which variation pattern from the upstream to the downstream does not show specific trends.

Three light non-metal elements, B, P, and S, exhibit sudden increases at the site 5-10j and its downstream sites, where populated and industrial zones are located and the treated industrial and municipal wastewaters are contaminated into the stream water (Figure 2). Similarly the concentrations of seven heavy metals, Cu, Cr, Ni, Zn, Ag, Au, and Hg, suddenly increase from the site 5-10j (Figure 3).

These sudden increases are probably caused by the enhancement of supplying elements through treated wastewater inflows. In particular the treated industrial wastewater is the main contamination source. A decrease of concentration at the inlet of treated municipal wastewater always show relative lower concentrations, which implies the inflow of treated municipal water is not the contamination source of these elements, or it has some removal (or attenuation) effects of heavy metals. The flux of Cu and Hg exhibits a peak value at sites 5-23e and 5-16e in the upper stream agricultural area (Figure 3).

However other heavy metals such as Ba, Mo, Cd, Sb, Tl, Pb, and toxic metalloids As and Se show no significant increases of the concentration at 5-10j and its downstream. The concentration variation of these elements generally show gradual increases toward downstream, while some peaks appear in the upstream (Figure 3).

The flux in the upstream is possibly due to an effect of agricultural chemicals, illegally disposed wastes, and natural (geological) origins.

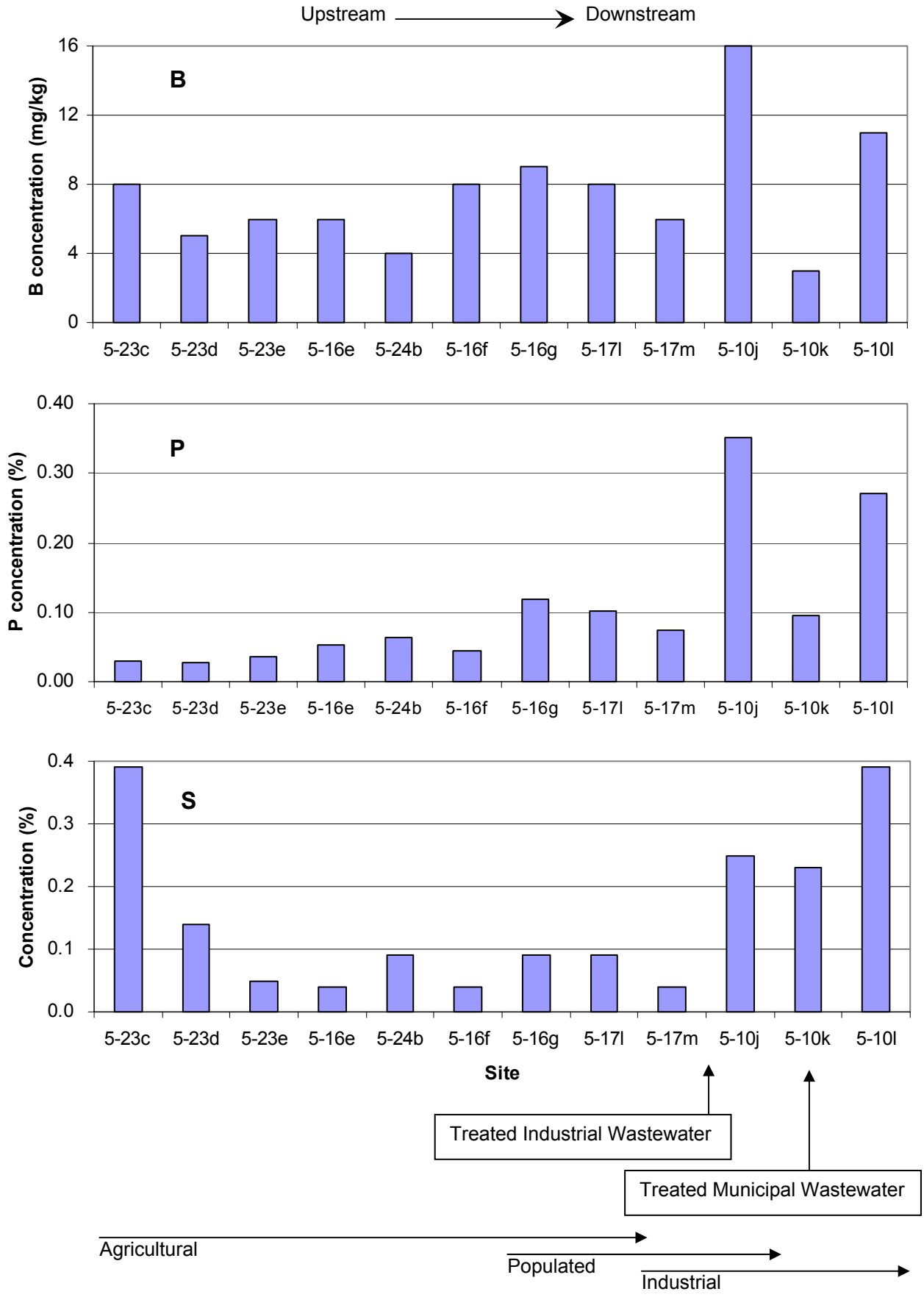

Figure 2: Variation of B, P, and S concentrations in stream sediments.

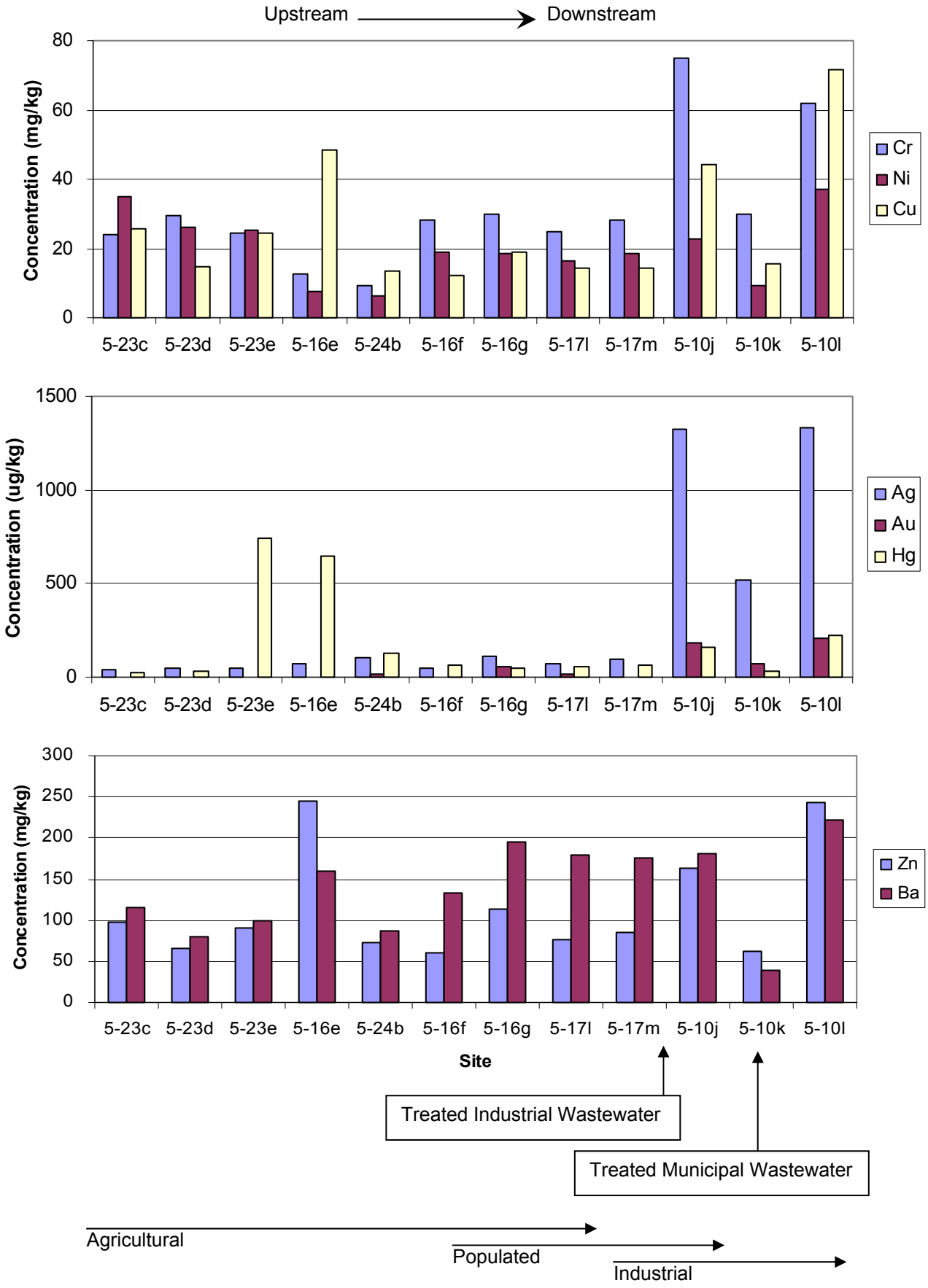

Figure 3: Variation of six PTEs (Cr, Ni, Cu, Ag, Au, Hg, Zn, Ba) concentrations in stream sediments.

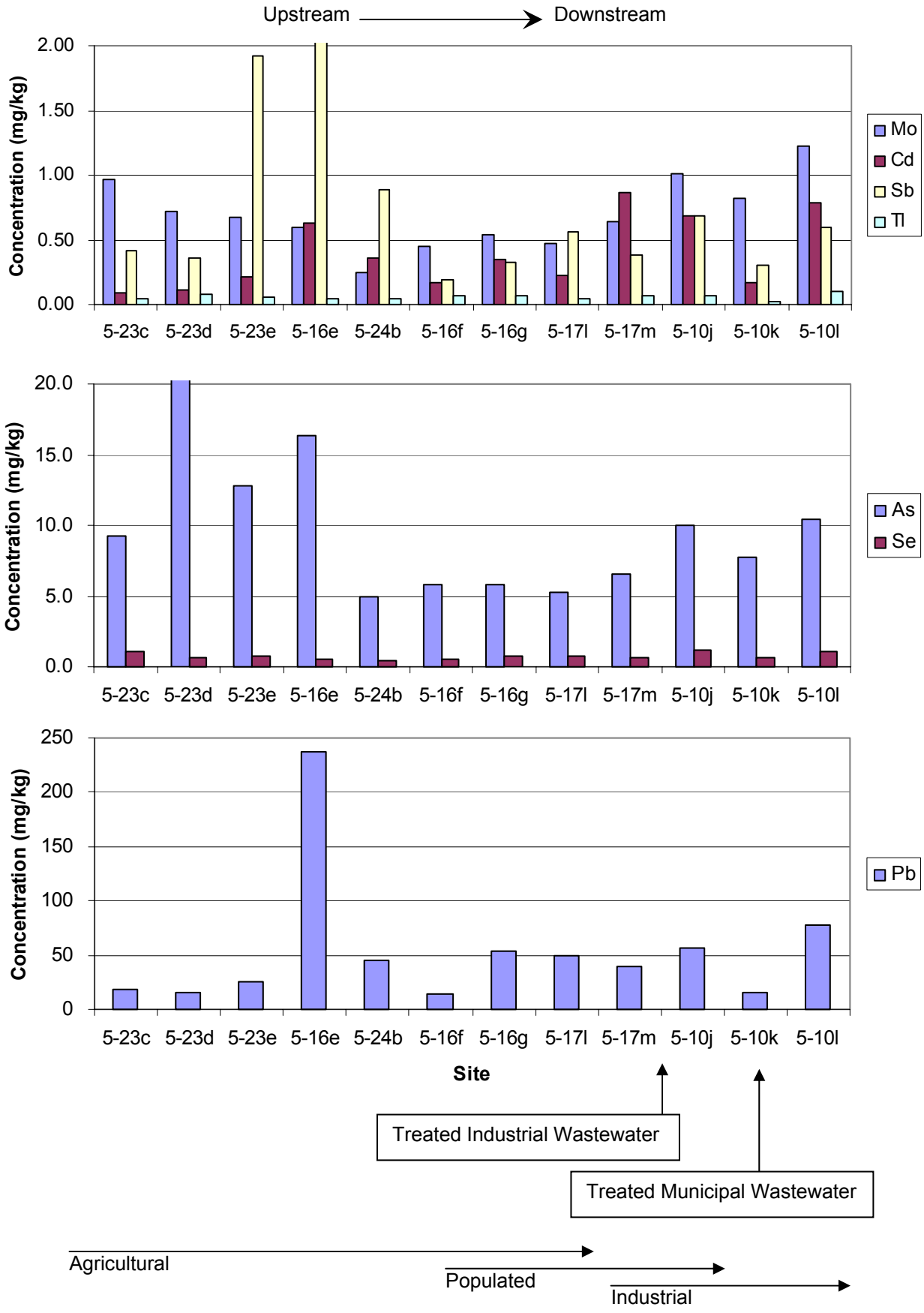

Figure 4: Variation of six PTEs (Mo, Cd, Sb, Tl, As, Se, Pb) concentrations in stream sediments.

Table 3: Several criteria for environmental screening of freshwater sediment contamination (unit: mg/kg except specified). Concentration values in the shaded cells are used for sediment contamination screening criteria in present study.

	NOAA SquiRTs for Freshwater Sediment*						Netherlands**			Japan
PTEs	Background		LTEL	TEL	PEL	UET	Ref.	Interv.	Test	EQS soil
Al	0.26%		2.55%							
Sb	0.16					3				
As	1.1		10.798	5.9	17	17	29	50	30	50
Ba	0.7						200	2000	400	
Cd	0.1-0.3		0.583	0.596	3.53	3	0.8	12	5	9
Cr	7-13		36.286	37.3	90	95	100	380	250	
Co	10						10	300	50	
Cu	10-25		28.012	35.7	197	86	36	190	100	
Fe	0.99-1.8%		18.84%							
Pb	4-17		37	35	91.3	127	85	530	150	600
Mn	400		630			1100				
Mo	10						10	200	40	
Hg	0.004-0.051			0.174	0.486	0.56	0.3	10	2	3
Ni	9.9		19.594	18	35.9	43	35	210	100	
Se	0.29									
Ag	<0.5					4.5				
Sn	5						20	300	50	
Tl	0.1-0.8									
U	0.7-9									
V	50									
Zn	7-38		98	123.1	315	520	140	720	500	

* NOAA Screening Quick Reference Tables (SQuiRTs) (NOAA, 1999). LTEL; Lowest ARCs H. azteca Threshold Effects Level, TEL: Threshold Effects Level, PEL: Probable Effects Level, UET: Upper Effects Threshold. The 'Background' values is obtained from fresh water sediments.
** Guide values and quality standards used in the Netherlands for assessing soil contamination. Ref.: Reference value, Interv.: Intervention value, Test: Test value (Alloway, 1995)
*** Critical soil total concentration: the range of values above which toxicity is considered to be possible (Kabata-Pendias and Pendias in Alloway,1995)
EQS soil: Environmental Quality Standards for Soil (Japan)

According to the criteria for sediment contamination (Table 3), the concentration of three PTEs, Hg, As, and Pb, exceeds the threshold values in the upstream area, where some harmful effects is presumed:

Hg: 5-23e (Jbal al Wost) and 5-16e (Mohamediyya)
As 5-23d (Jbal al Wost) and 5-16e (Mohamediyya)
Pb: 5-16e (Mohamediyya)

The most polluted site 5-16e is located at the south to Mohamediyya town, where a lot of solid waste are illegally diosposed and accumulated. The direct pollution source is probably the solid wastes. Agricultural chemicals are also considered to be the pollutants because the sites are located in widely-developed agricultural zone.

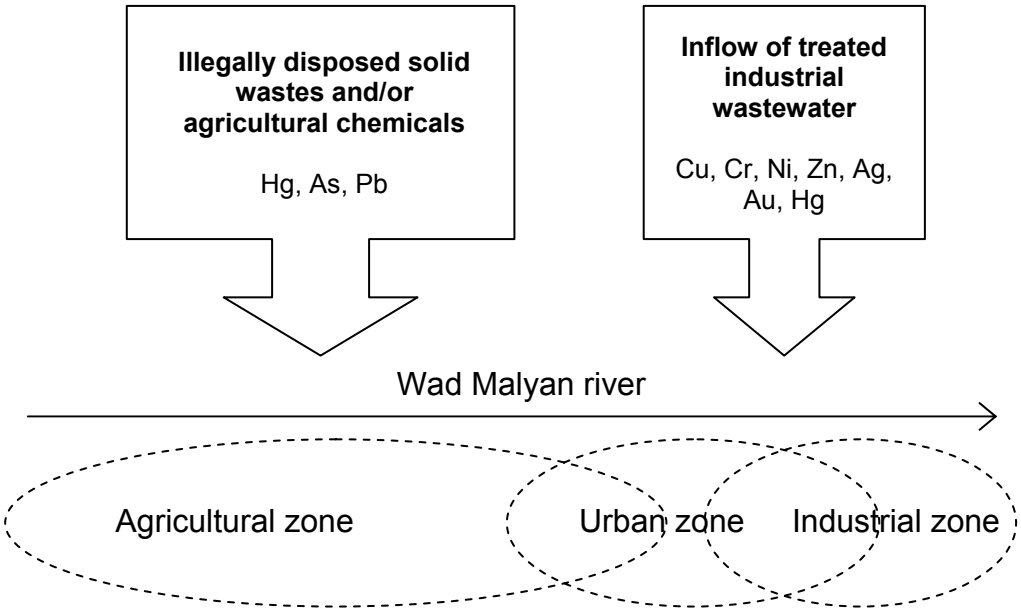

Figure 5: Schematic diagram of the sediment contamination sources along the Wad Malyan river

V. Conclusions

(1) Chemical composition of the Wad Malyan stream sediments was examined using aqua regia extraction method.
(2) .The concentration of major elements such as Na, Mg, Al, K, Ca, and Fe, is around background level, of which variation pattern from the upstream to the downstream does not show specific trends.
(3) Non-metal light elements, B, P, and S, and seven heavy metals, Cu, Cr, Ni, Zn, Ag, Au, and Hg, exhibit sudden increases at Ezzahra and its downstream, where populated and industrial zones are developed. The inflow of treated industrial wastewater is the possible source of the contamination.
(4) However other heavy metals such as Ba, Mo, Cd, Sb, Tl, Pb, and toxic metalloids As and Se show no significant increases of the concentration at Ezzahra and its downstream.
(5) The concentration of three PTEs, Hg, As, and Pb, exceeds the threshold values in the upstream area, from Jbal al Wost to Mohammediyya, which is probably due to illegally disposed solid wastes in the river.

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