 Japan International Cooperation Agency

## [ Characterization of Metal/Metalloid Pollution in Oued El Harrach Sediments ]

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11<sup>th</sup> February 2007, Ministry of Land Management and  
Environment, Algeria

## [ Plan of the Presentation ]

- Previous Results (2004-2006) :  
Environmental Pollution Monitoring in Oued El Harrach and the Bay of Alger, with special reference to mercury contamination
- New analytical data from Upstream sediments
- Characterization of heavy metal/metalloid contamination
- Conclusions
- Recommendations

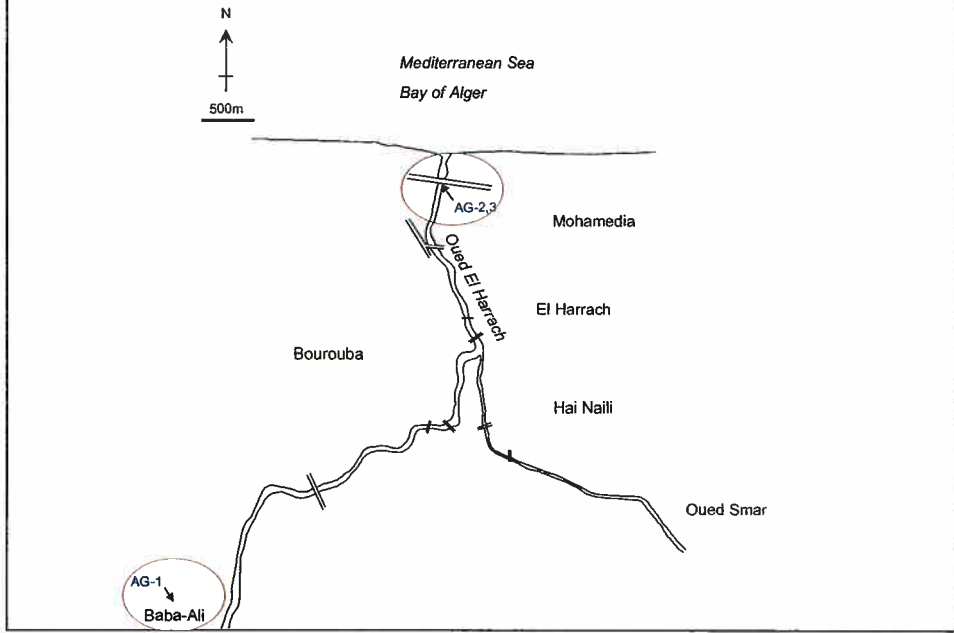
## Environmental Pollution in Oued El Harrach A Technical Cooperation between ONEDD & JICA

- February 2003: Preparatory Study
  - Test sampling of sludge and sediment
  - Chemical analysis of sludge and sediments
- January 2004: 1<sup>st</sup> Collaboration
  - Equipping on-site water multiprobe analysis
  - Sampling of Oued El Harrach water
  - Chemical analysis of river water
- October 2004: 2<sup>nd</sup> Collaboration
  - Inspection of factory with Wilaya inspectors
  - Bottom-sediment sampling in Oued El Harrach
  - Chemical analysis of wastewater
  - Mineralogical and SEM study of sediments
- March-April 2005: 3<sup>rd</sup> Collaboration
  - Installation of instrument, an Atomic Adsorption Spectrometer
  - Offshore and onshore sampling
  - Chemical analysis of wastewater, water, and sediments
- December 2005-: Technical Cooperation Project
  - Technology transfer and collaboration

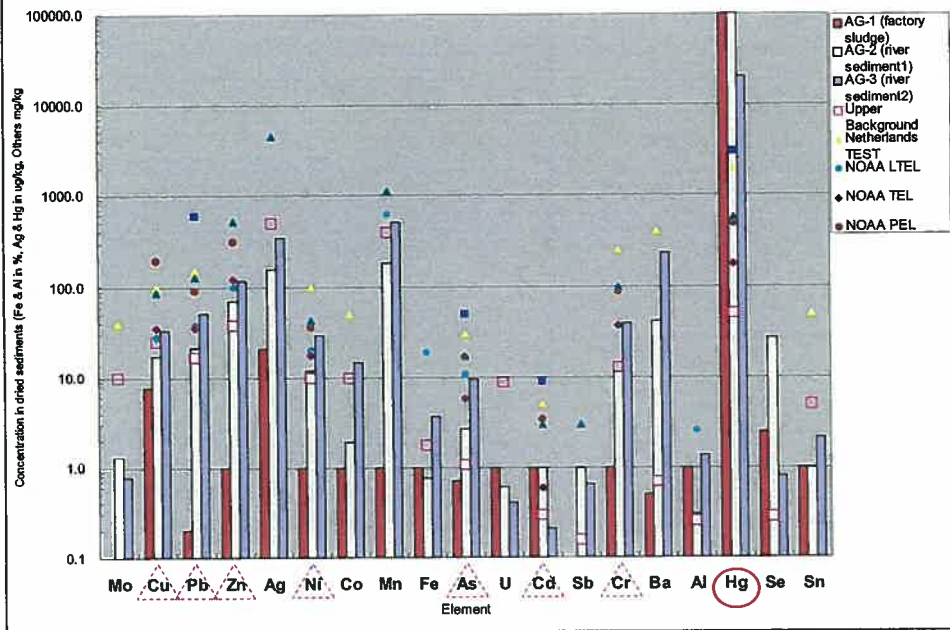
*Finding of  
severe Hg  
pollution in  
water and  
sediments*



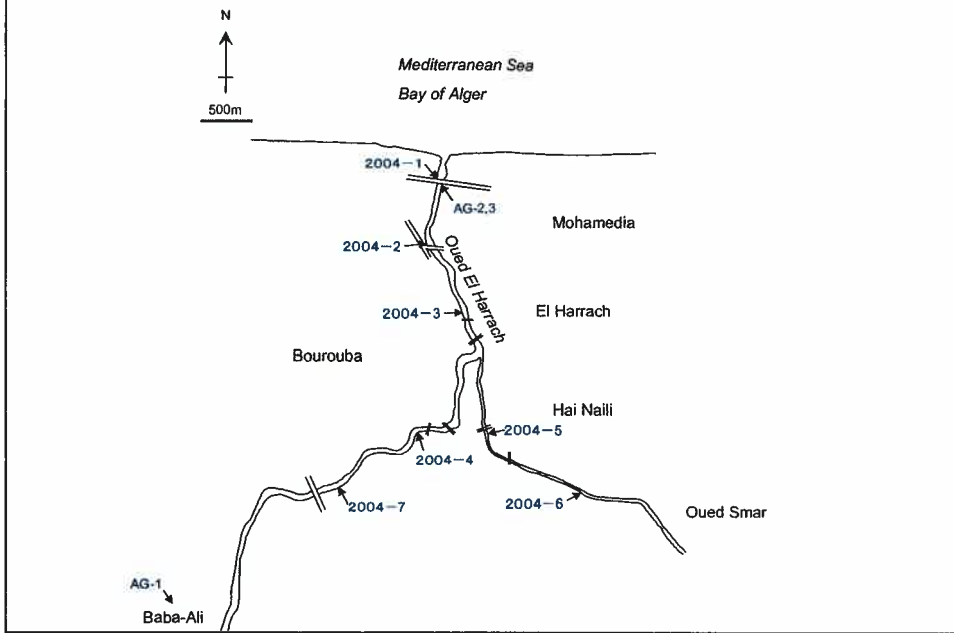
### Sites in 2003 Test Sampling of Sediments and Sludge



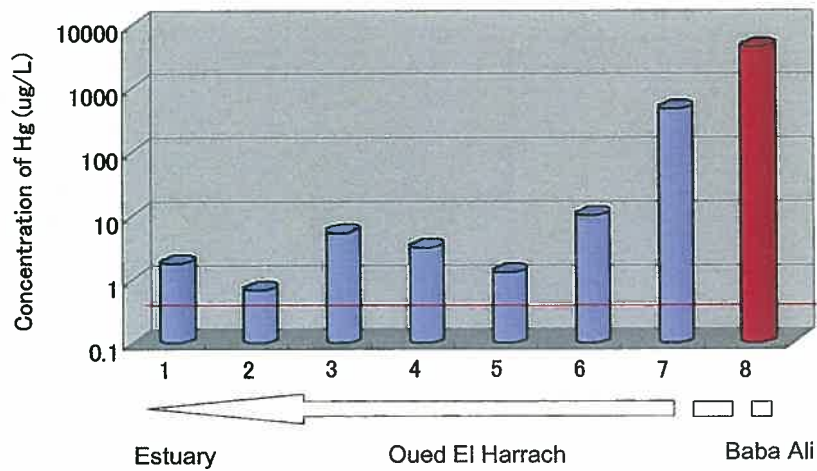
### Potentially toxic elements (PTEs) concentration in Oued El Harrach sediments and wastewater sludge from a chlorine factory – by Yoshida(2003)



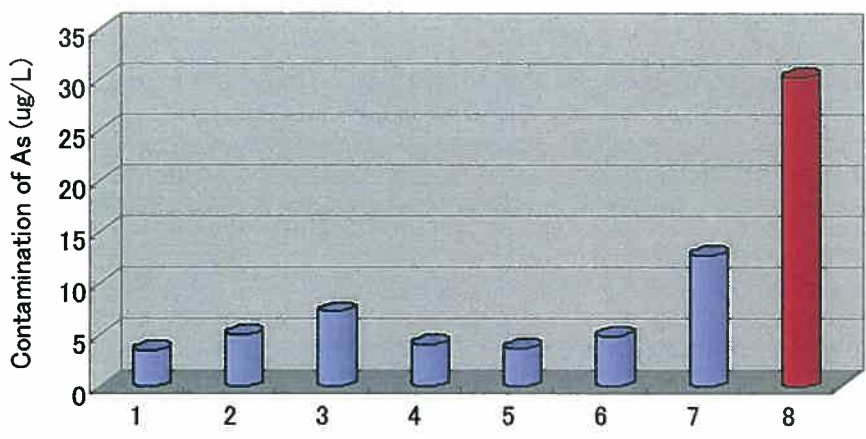
### Sites for Water Sampling along Oued El Harrach



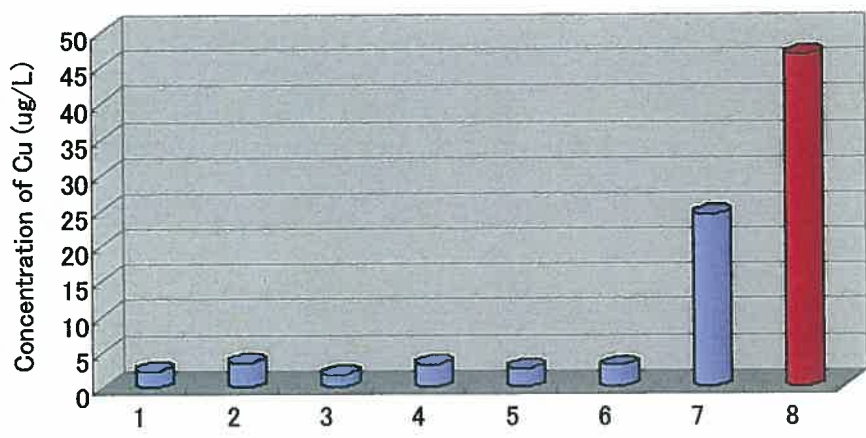
### Variation of Hg Contamination along Oued El Harrach

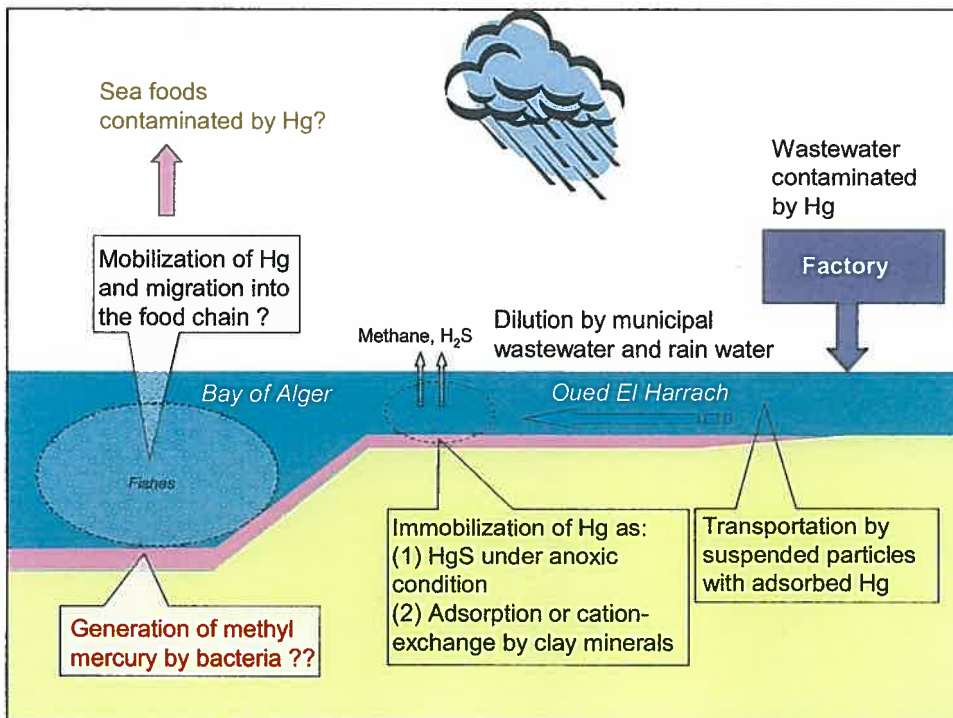
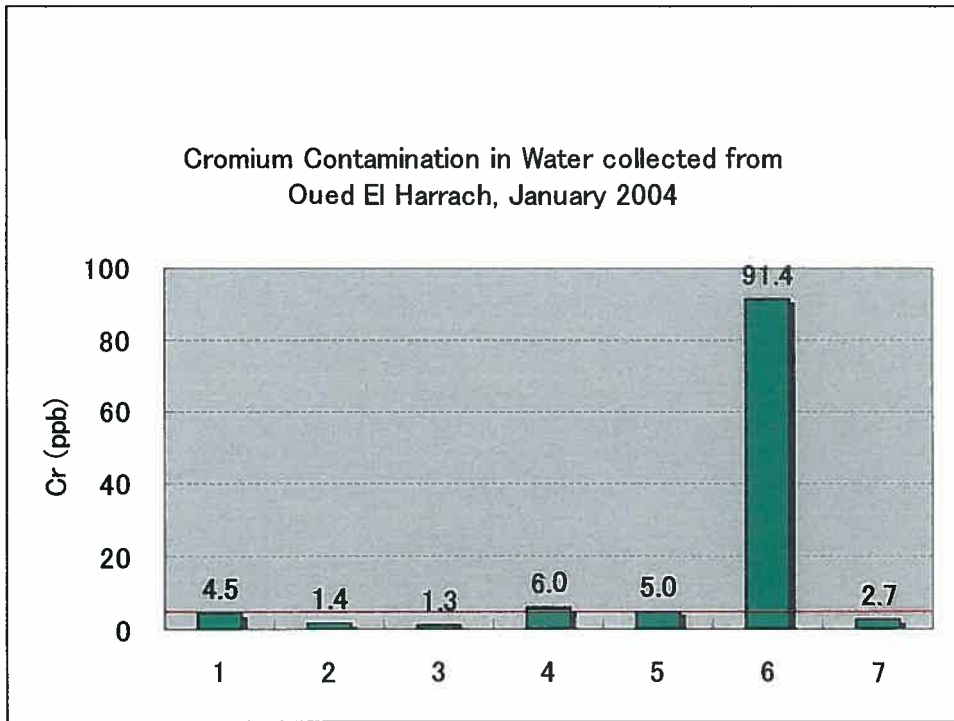


### Variation of As contamination along Oued El Harrach



### Variation of Cu contamination along Oued El Harrach





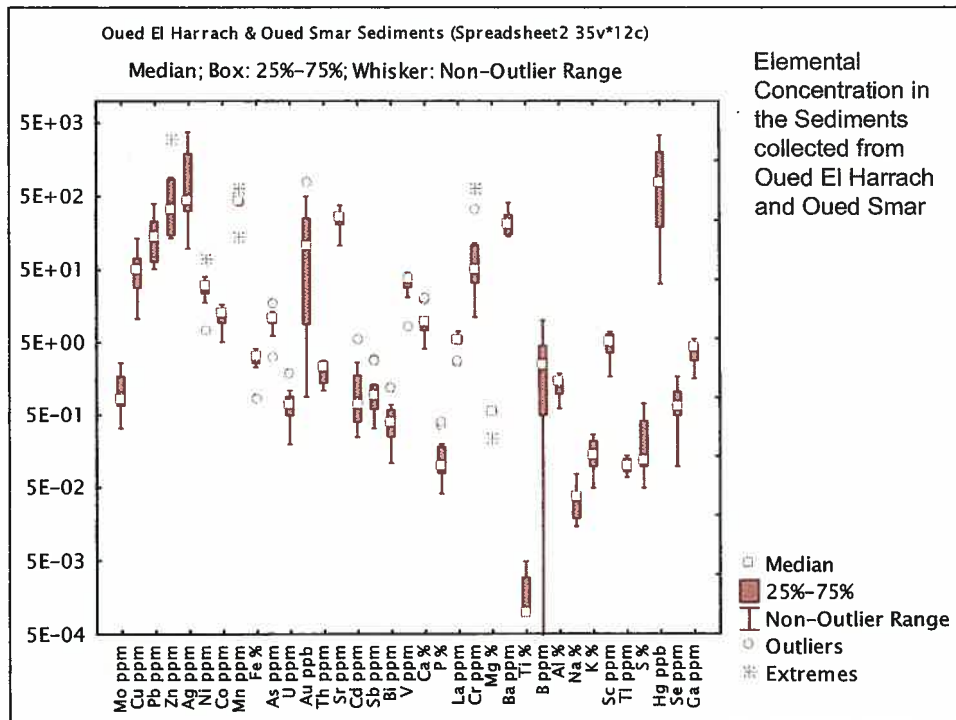


## Sediment Contamination Upstream of Oued El Harrach

- OEH-01 estuaries
- OEH-02 Mohammedia
- OEH-03 El Harrach
- OEH-04 Baraki
- OEH-07 Baba Ali
- OEH-08 Sidi Moussa
- OEH-09 Dour Abuziz
- OEH-10 Bougara
  
- OEH-05 Baraki east
- OEH-06 Smar west
- OS-01 Oued Smar Industrial
- OS-02 Oued Smar Airport

## Analytical Procedure

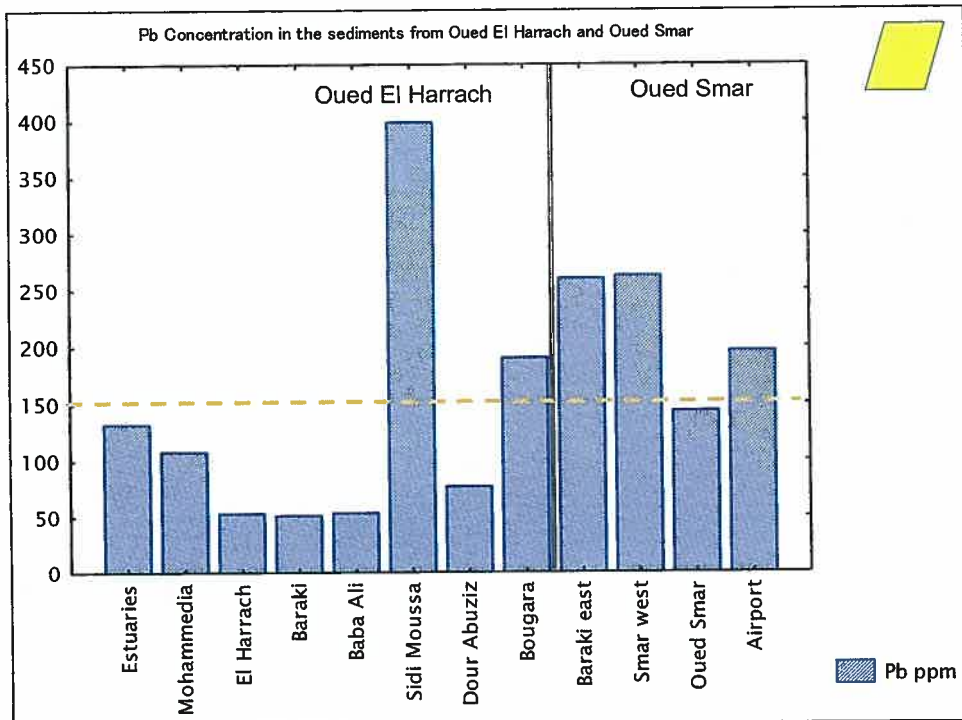
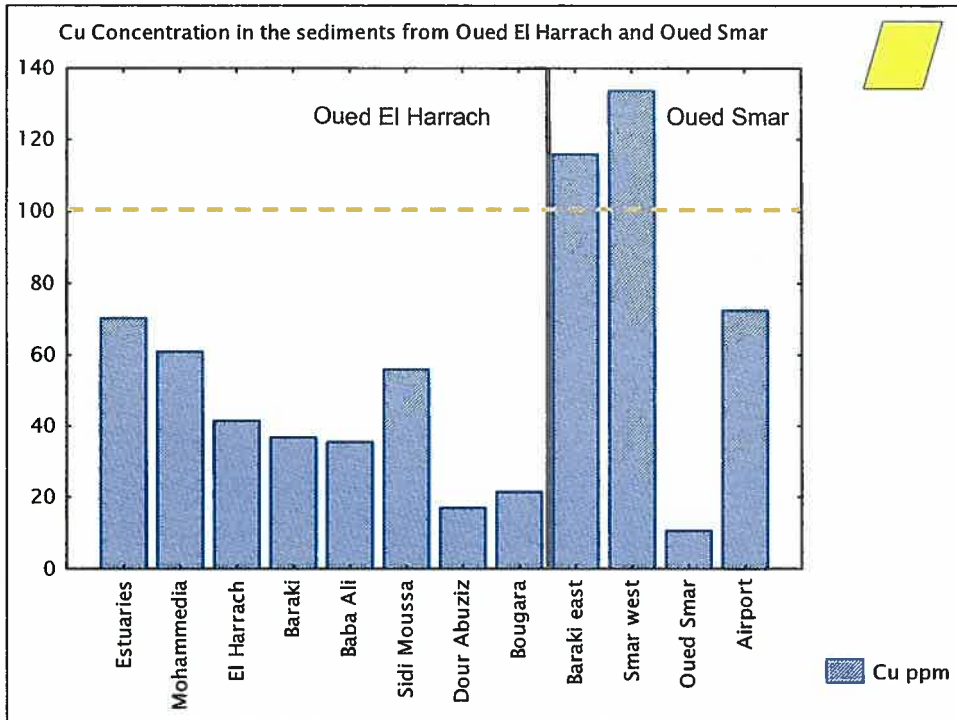
- 1.00 gm sample split
- Extracted with Aqua Regia
  - 3 ml HCl-HNO<sub>3</sub>-H<sub>2</sub>O
  - at 95 degree Celsius
  - for one hour
- Diluted to 10 ml
- Analyzed by ICP/ES & MS
- 37 elements

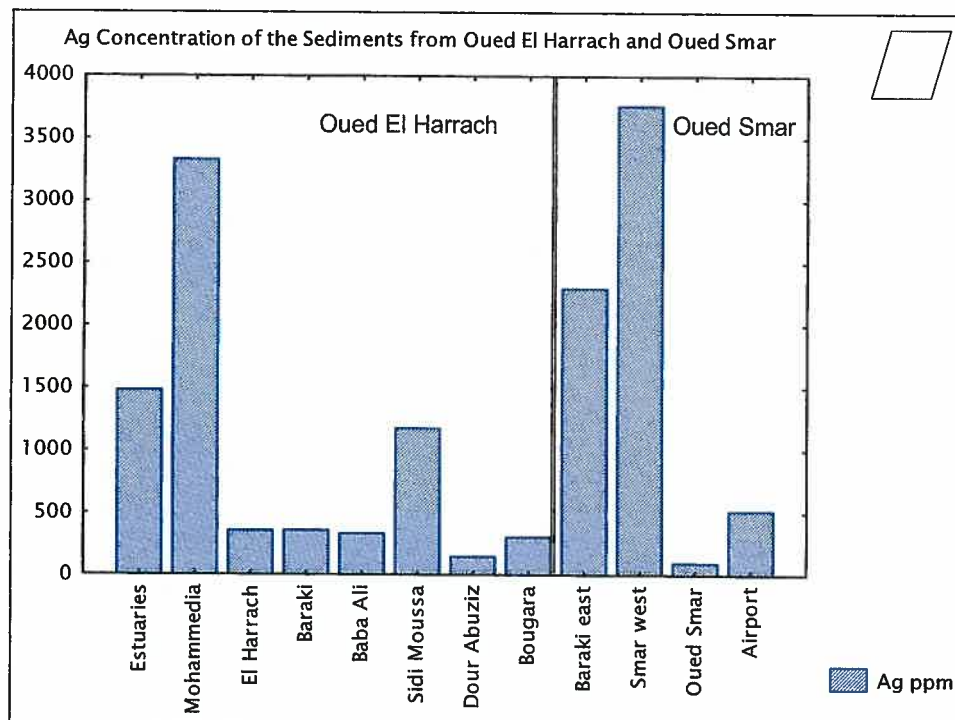
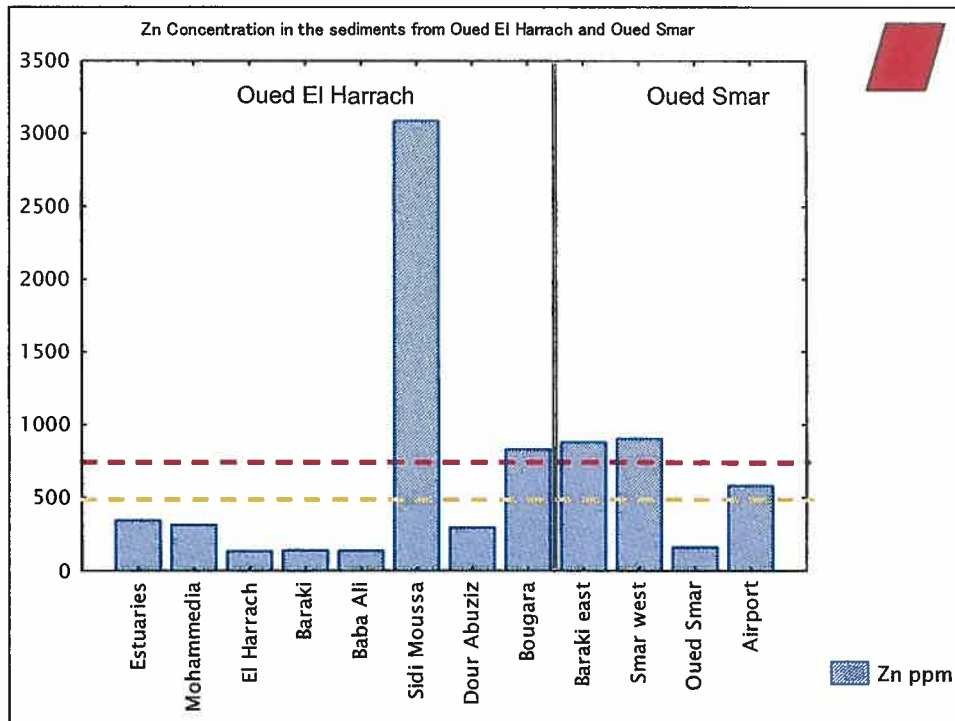


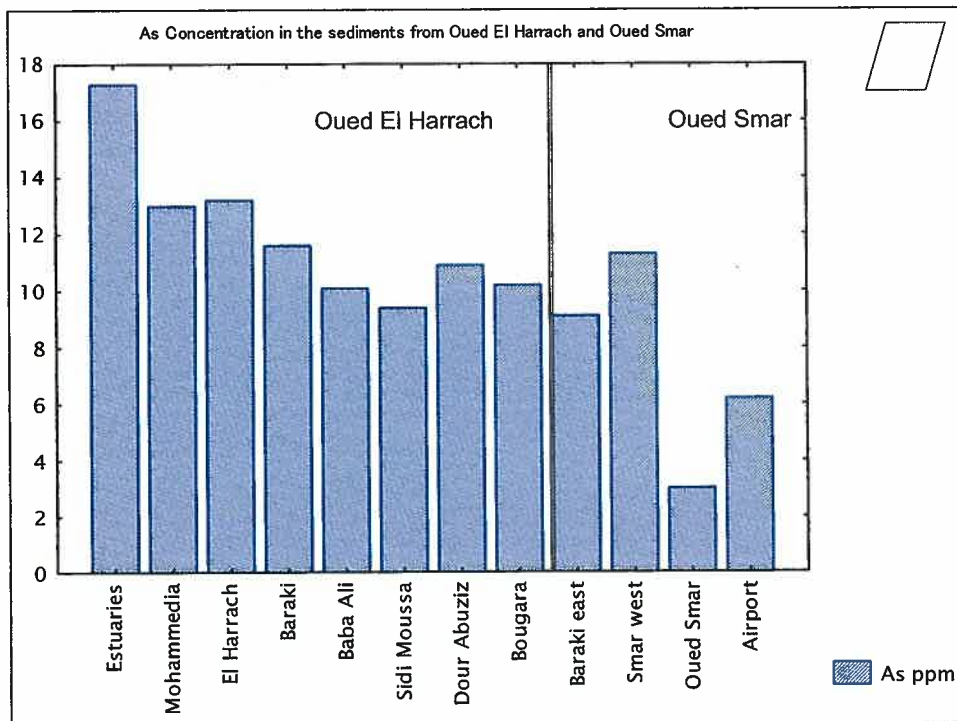
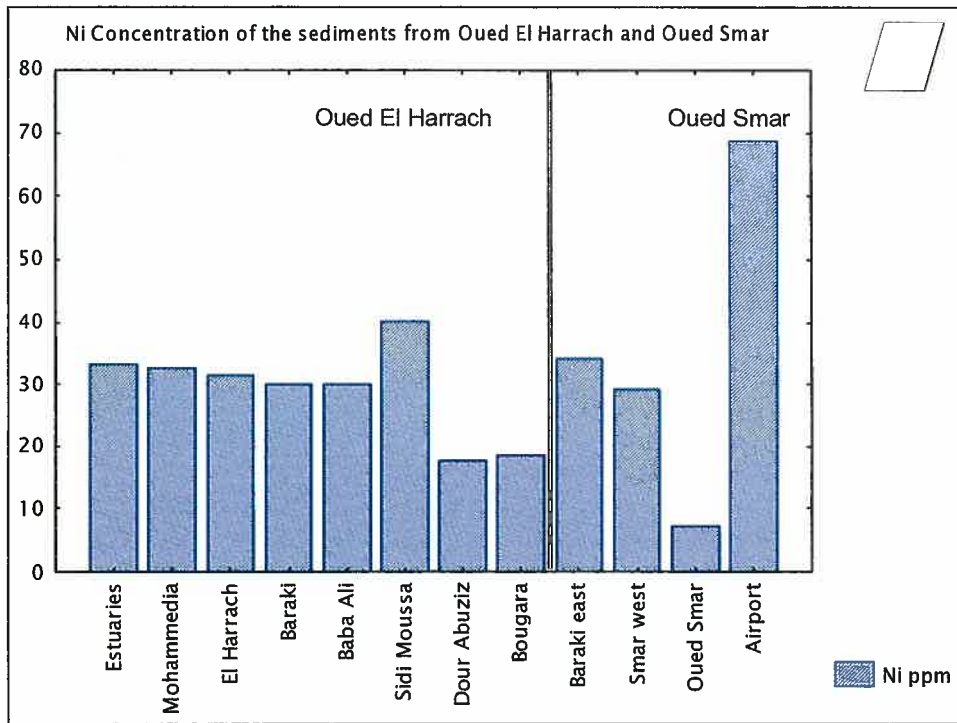
## Descriptive Statistics of Analytical Results and Criteria for Sediment Pollution

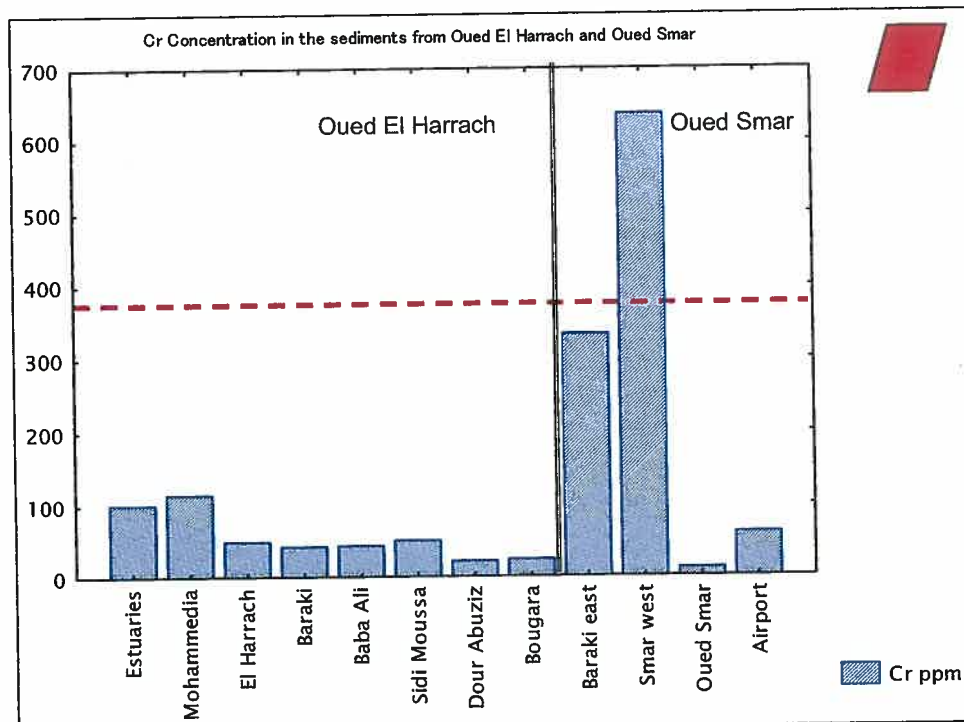
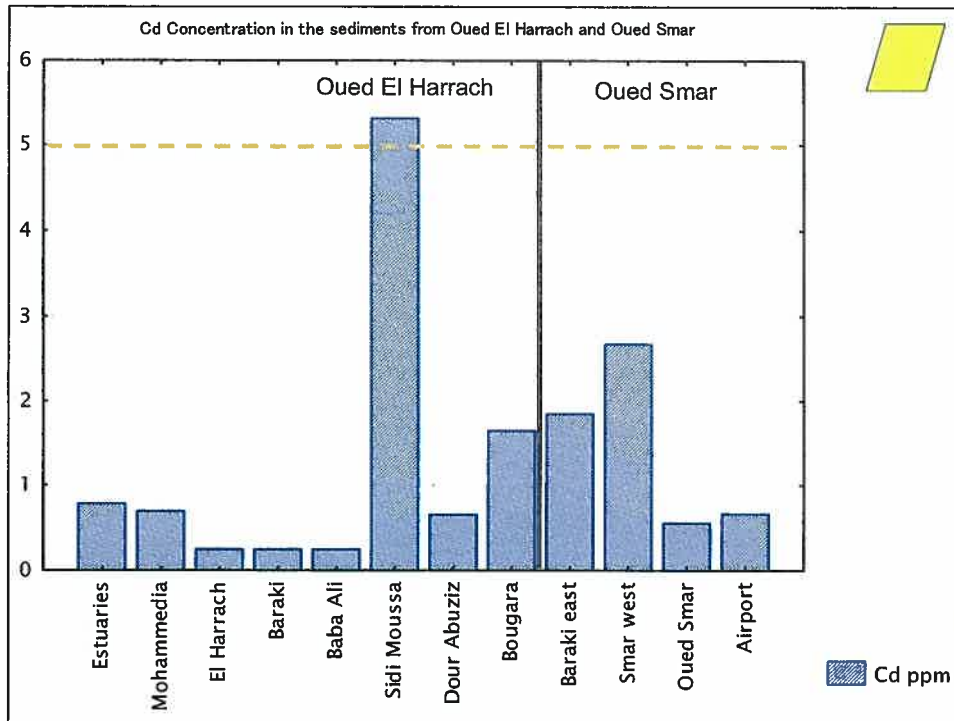
PTEs	Descriptive Statistics Oued El Harrach & Oued Smar sediments					NOAA	Criteria1	Criteria2
	Mean	Minimum	Maximum	StdDev.	Background			
Mo ppm	1.216	0.3300	2.640	0.764		10	40	200
Cu ppm	56.048	10.6100	133.790	38.030		25	100	190
Pb ppm	160.533	51.1900	399.200	106.768		17	150	530
Zn ppm	650.692	134.6000	3090.300	824.303		38	500	720
Ag ppm	1180.583	97.0000	3765.000	1285.549		0.5	4.5	
Ni ppm	31.067	7.2000	68.800	14.869		9.9	100	210
Co ppm	11.567	5.1000	16.600	3.256		10	50	300
Mn ppm	422.833	140.0000	652.000	112.772		400	1100	
Fe %	2.998	0.8300	4.120	0.864		1.8	18.84	
As ppm	10.442	3.0000	17.300	3.566		1.1	30	50
U ppm	0.750	0.2000	1.800	0.417		9		
Cd ppm	1.302	0.2500	5.320	1.469		0.3	5	12
Sb ppm	1.153	0.3300	2.840	0.833		0.16	3	
V ppm	33.250	8.0000	46.000	10.746		50		
Cr ppm	124.450	11.2000	637.400	183.208		13	250	380
Ba ppm	230.258	143.4000	411.600	86.950		0.7	400	2000
Al %	1.292	0.6200	1.860	0.426		0.26	2.55	
Ti ppm	0.104	0.0700	0.140	0.024		0.8		
Hg ppb	1113.750	32.0000	3439.000	1104.607		51	2000	3000
Se ppm	0.767	0.1000	1.700	0.452		0.29	50	300

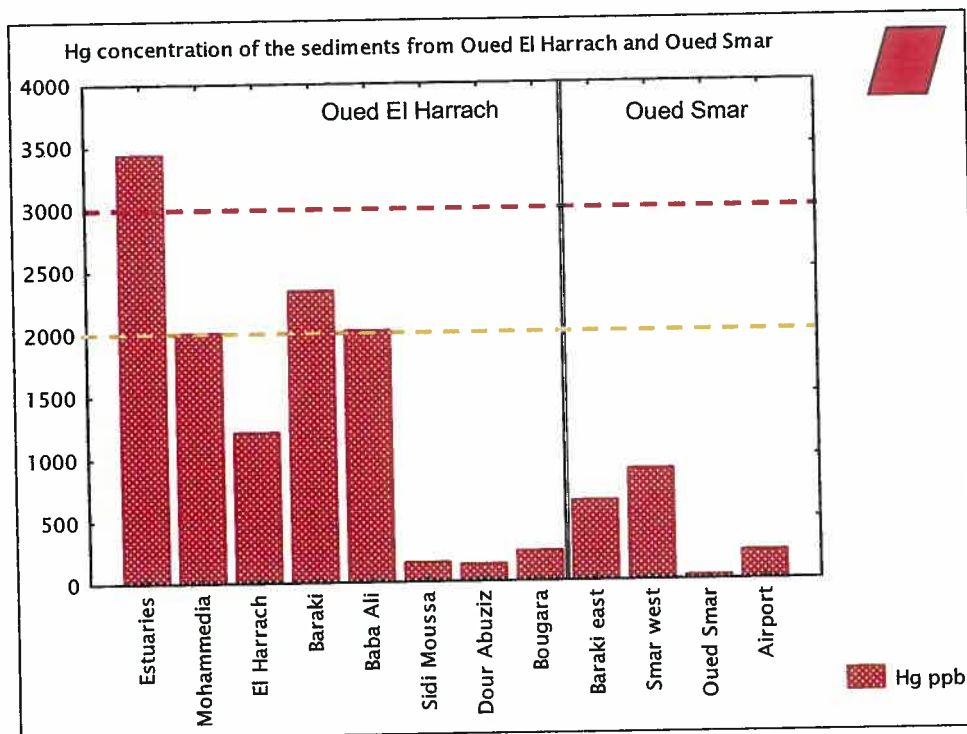
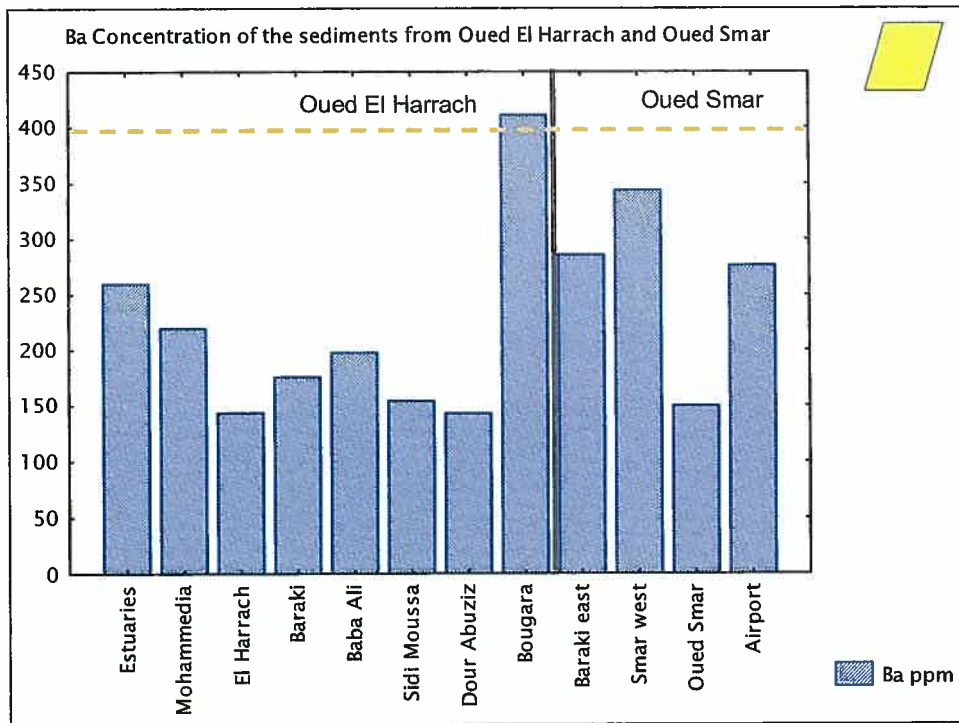




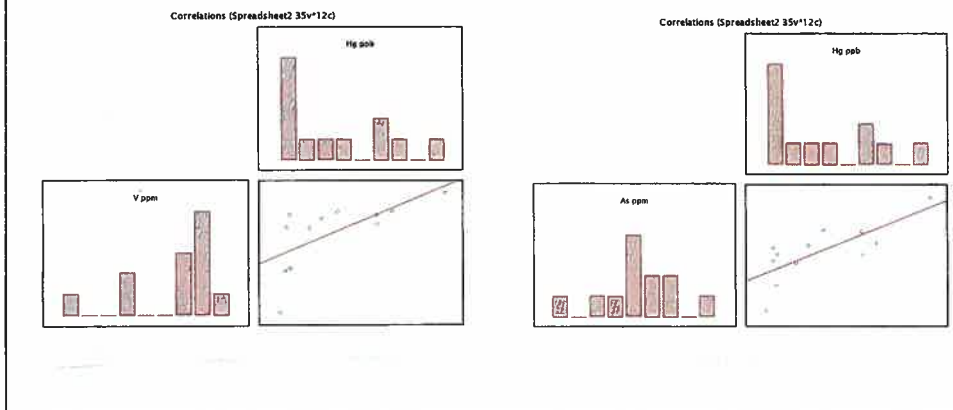








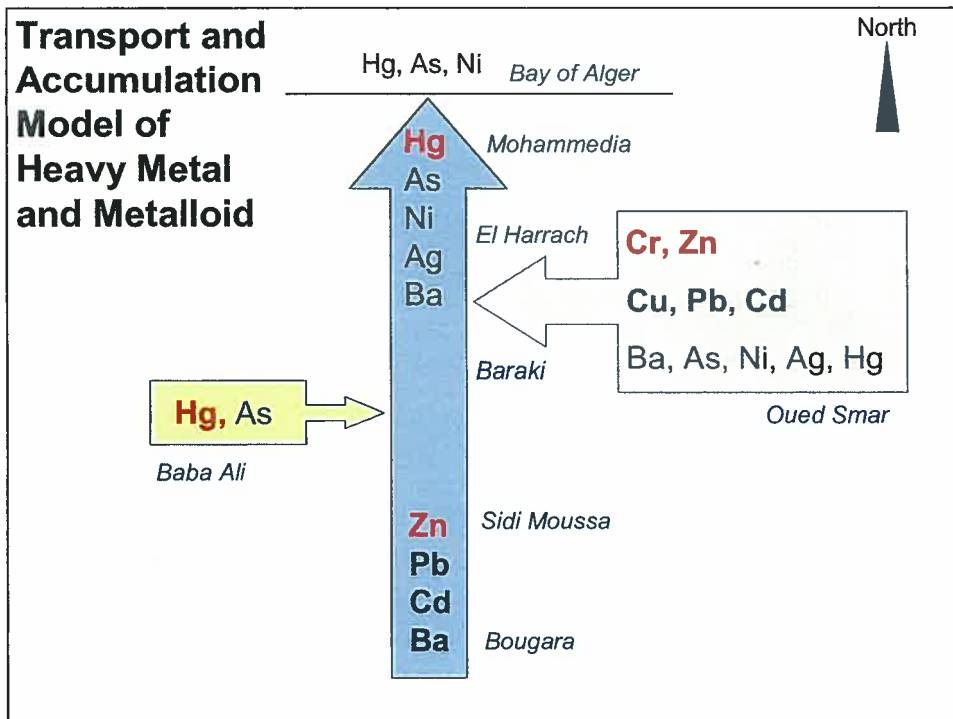
## [ Hg-As-V Correlation ]



## [ Characteristics of Pollution Sources ]

- Upstream of Oued El Harrach (Bougara-Sidi Moussa-Baraki)
  - **Zn**
  - **Ba, Cd, Pb**
- Baba Ali Industrial zone
  - **Hg**
  - **As**
- Oued Smar Industrial Zone
  - **Cr, Zn**
  - **Pb, Cd, Cu, As, Hg, Ni, Ba, Ag**
- Downstream of Oued El Harrach (Baraki-Mohammedia)
  - **Hg**
  - **Ba, Ni, As, Ag**





[ Sludge in wastewater drain shows extraordinary high concentration of Hg ]



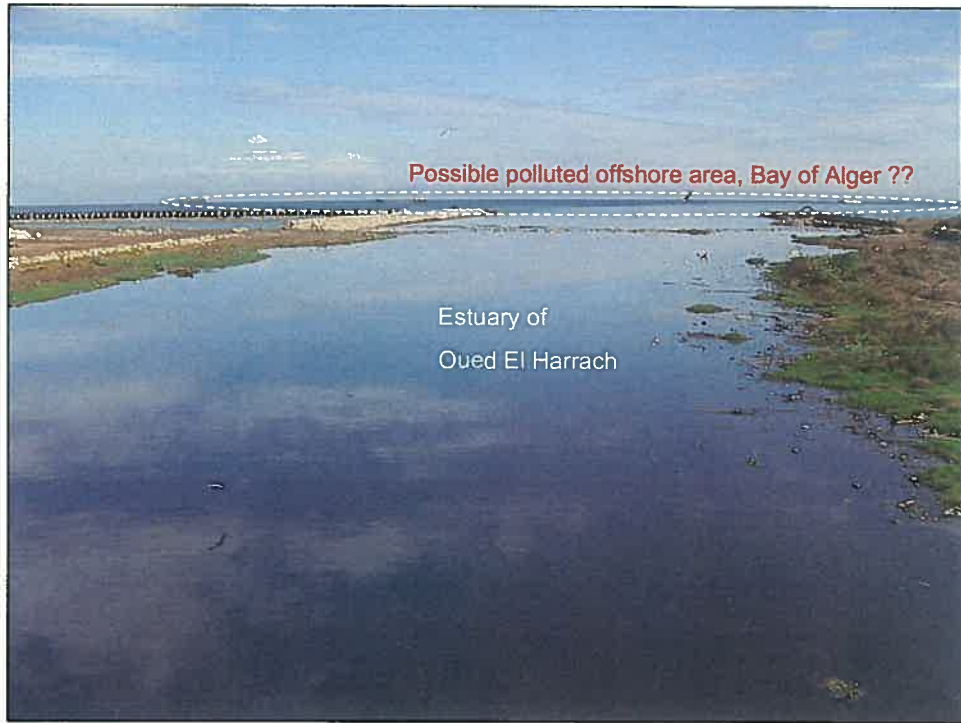
Wastewater is discharged directly into the river without any treatment

Polluters



### Heavy Metals in the Industrial Wastewater Samples: An Assessment

Paramètre	Cd*	Cr	Cu	Pb	Ni	Zn	Hg
Unité	mg/l						µg/l
ENAP	<<	<<	<<	<<	0.022	<<	12.11
ENMTP unité matériel de béton d'El Harrach	<<	<<	<<	0.20	0.047	0.012	8.36
ENPC 1	0.008	<<	2.220	0.27	0.039	<<	3.14
ENPC 2	0.012	<<	<<	0.12	0.011	<<	12.00
ENPEC unité accumulateurs	<<	<<	0.056	0.42	0.020	<<	10.23
Tannerie Semmache Ahmed	0.012	60.43	0.029	0.43	<<	<<	11.04
Tannerie Kehri dahmane	<<	0.54	<<	1.20	0.007	<<	7.96
EMB1	<<	<<	0.492	2.40	0.069	1.470	21.21
EMB2	<<	<<	1.890	0.45	0.047	0.596	3.54
Ets Kehri dahmane	<<	0.97	0.360	0.44	0.024	<<	7.28
AGENOR	<<	0.15	8.860	0.74	0.266	1.081	16.93
RAFFINERIE D'ALGER	<<	<<	<<	<<	<<	<<	18.00
Saidal Société de produits médicament	<<	<<	<<	0.18	0.029	<<	1.50
Catel 1	<<	<<	4.840	1.15	0.041	0.680	<<
Catel 2	<<	<<	0.220	0.19	<<	<<	<<
Aventis pharmaceutique	<<	<<	0.710	0.27	0.021	0.710	<<
IAP	<<	<<	<<	0.36	<<	<<	<<
Soachlore (GIPEC)	---	---	---	---	---	---	5,719.44
Valeur maximal admissible	0.2	0.1	3	1	5	5	10





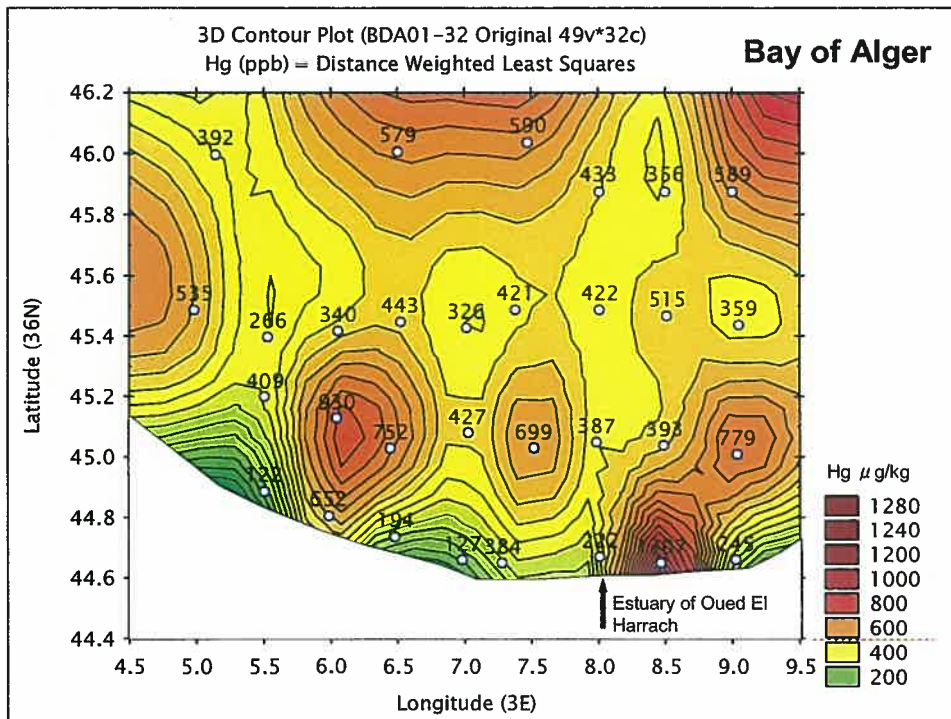


ONEDD-JICA Offshore Survey Team



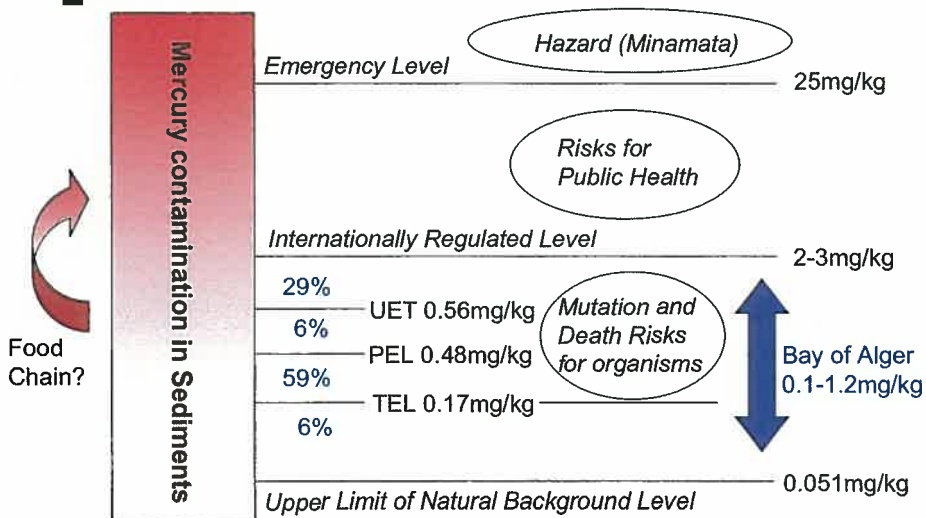
Water sampling



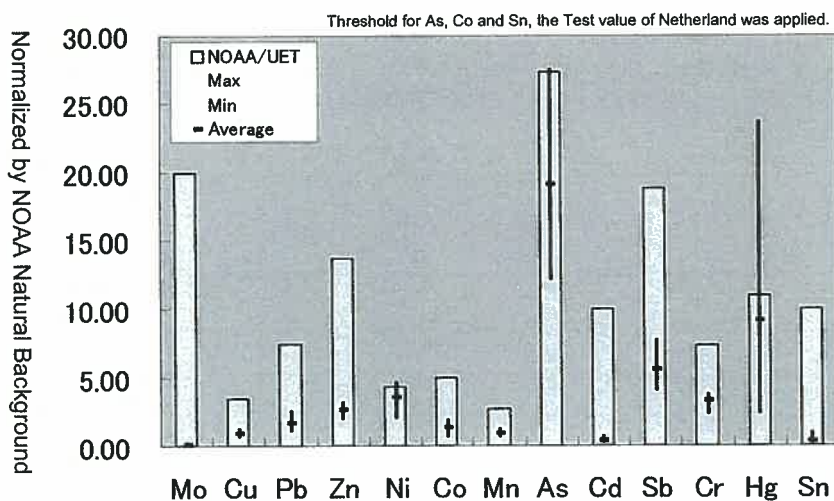


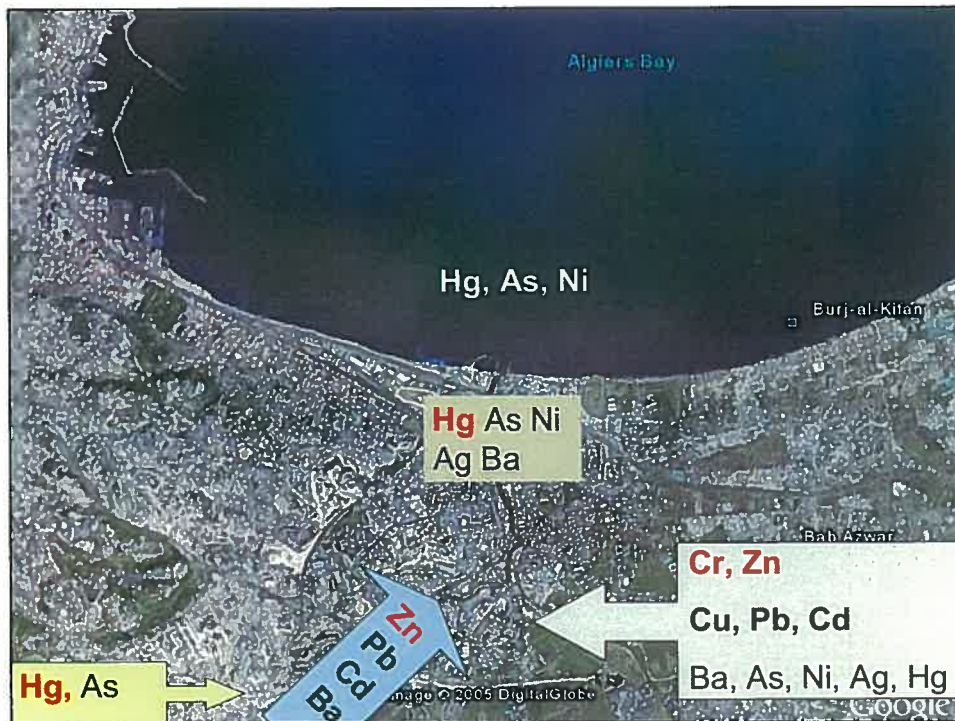


## Summary of the Results: Sediment Contamination by Mercury



## Toxic Metals and Metalloids in the Sediments of bay of Alger





## [ Conclusions: ]

- Heavy metal/metalloid contamination of sediments in Oued El Harrach can be characterized in separated four areas: Upstream, Baba Ali, Oued Smar, and Downstream areas.
- These four are individually determined by unique combination of concentrated potentially toxic elements:
  - Upstream: Zn > Pb, Cd, Ba
  - Baba Ali: Hg >> As
  - Oued Smar: Cr, Zn > Cu, Pb, Cd > As, Hg, Ni, Ag, Ba
  - Downstream: Hg >> As, Ni, Ag, Ba
- They are probably contaminated by various effluents from surrounding industrial activities.
- The concentration of Hg, Cr, and Zn, have been determined as hazardous level for public health, and that of Cu, Pb, and Cd as warning level.

## Heavy Metals in the Industrial Wastewater Samples: An Assessment

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Valeur maximal admissible	0.2	0.1	3	1	5	5	10

## Recommendations

- It is recommended to analyze all industrial effluents (wastewater and solid waste) generated in the area.
- According to the analytical results, point and non-point sources of pollutants should be identified, in particular, for Hg, Cr, Zn, Cu, Pb, and Cd.
- It is recommended to study a model of pollutant migration, transport, chemical material balance and accumulation process.
- Appropriate countermeasure (de-pollution) should be studied based on the risk assessment.

## De-pollution Project Two Targets

High Priority

- Polluter/Source Control
  - Mitigation of pollutants from polluters
  - Legal Basis: Effluent Regulations and Enforcement system
  
- Remediation of Polluted Site
  - Decontamination of the site (factory sites, river, coast, and surroundings)
  - Legal Basis: Environmental Quality Standard (EQS) and Hazardous Waste Guideline

Not yet defined in Algeria

## Project Mid-Term Evaluation

A Summary

## Mid-Term Evaluation Based on Proposed Outputs of PDM

- |                                 |             |
|---------------------------------|-------------|
| ■ Output 1: Lab Management      | Delay       |
| ■ Output 2: Survey and sampling | On schedule |
| ■ Output 3: Organic chemistry   | Delay       |
| ■ Output 4: Inorganic chemistry | On schedule |
| ■ Output 5: Microbiology        | (Planned)   |
| ■ Output 6: Database            | On schedule |
| ■ Output 7: Interpretation      | Planned     |
| ■ Output 8: Depollution         | Planned     |

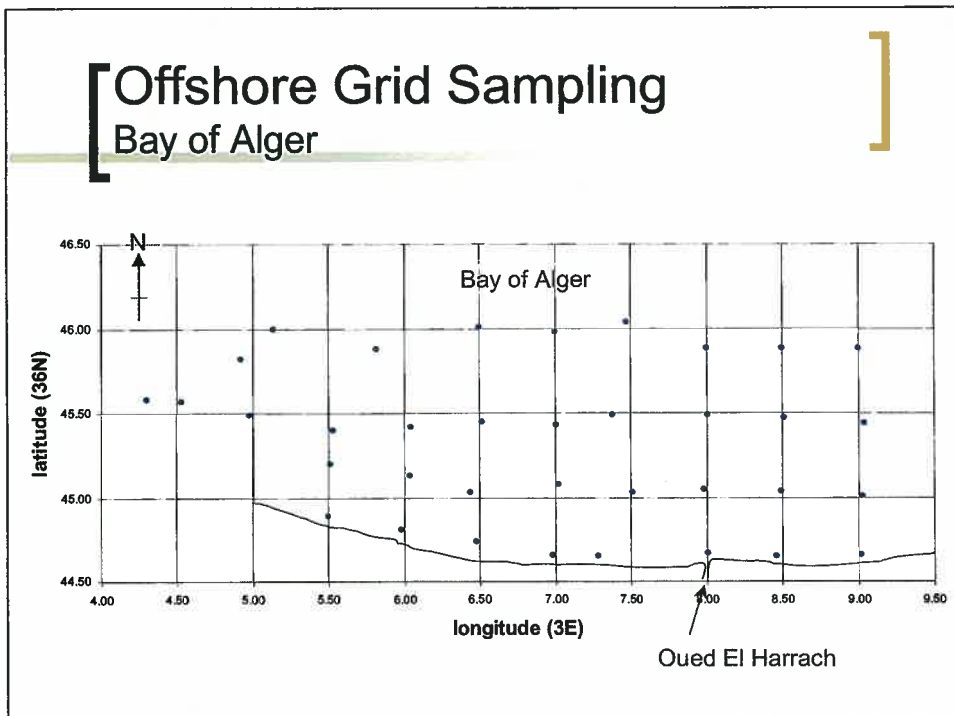
## Mid-Term Evaluation Conclusions

- At mid-point of the Project, the performance for achieving Project Purpose defined by the PDM shows fairly appropriate progress in technical side, in particular field monitoring/sampling (Output 2) and inorganic chemical analysis (Output 4), but rather inappropriate in administrative/management side (Output 1).
- Thus the performance of the project is almost in line with the plan only in technical side.
- The Project Purpose, as evaluated by the original indicators, is not likely to be achieved by the end of the project term unless appropriate number of laboratory staff, laboratory management system and proposed facilities are provided by the Algerian side.

## Mid-Term Evaluation Recommendations

- Improve laboratory facility
  - Construction of an intermediate laboratory
  - Repair of gas chromatography
- Improve laboratory administration/management
  - Management system and human resource
  - Job description and coordination
  - Regular meetings
- Enhance analytical techniques
  - Organic chemistry
  - Microbiology
  - Quality control
- Increase the inputs from JICA about environmental quality standard and de-pollution issues
  - Series seminar in July 2007 in MATE
- From technology transfer to collaboration
  - Interpretation skills
  - Collaboration with Wilaya Environment department



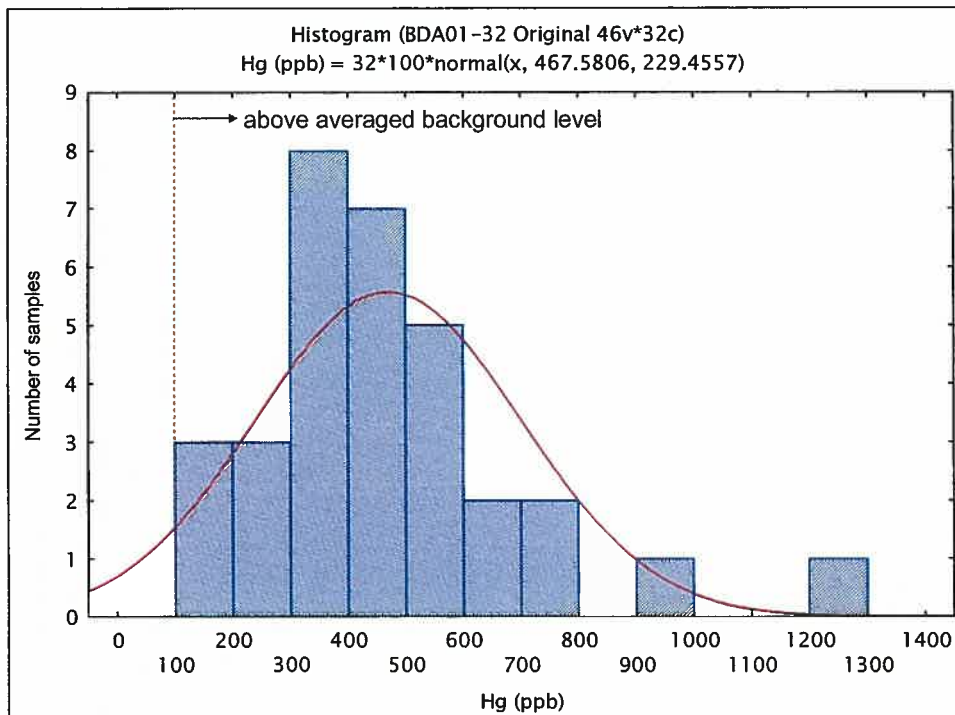






# Aqua Regia Extraction

- HCl-HNO<sub>3</sub>-H<sub>2</sub>O
- 95°C, 1 hour
- ICP-MS analysis
- Total 32 samples




PTEs	NOAA SQUIRTs for Freshwater Sediment*					Netherlands**			Japan
	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	

Criteria for Screening Sediment Contamination

Mercury

[ NOAA Screening Quick Reference Tables (SQUIRTs) ]

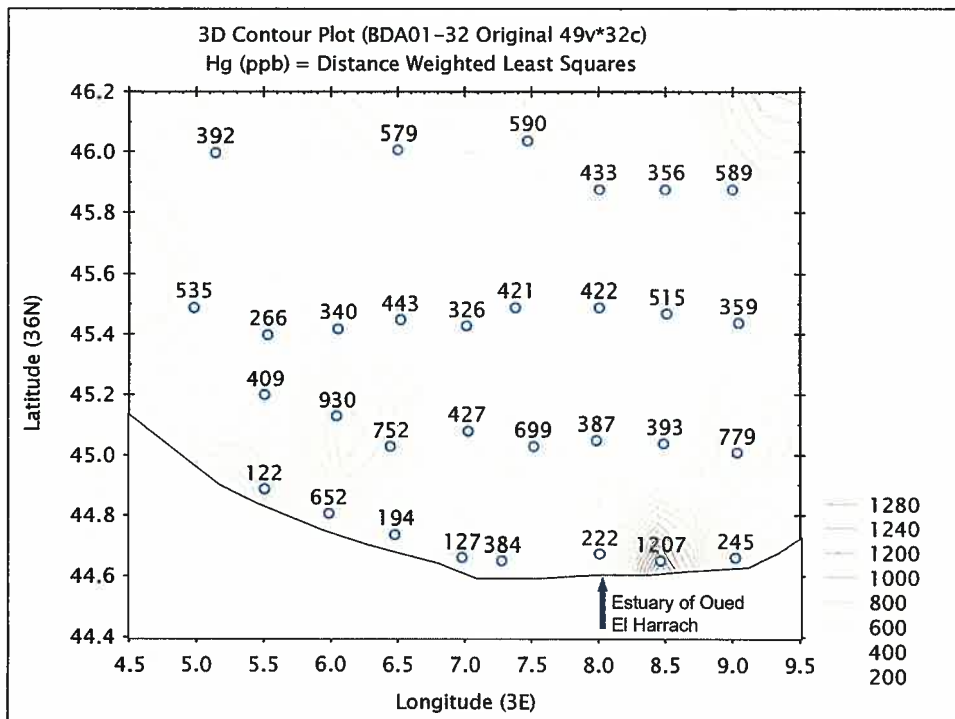
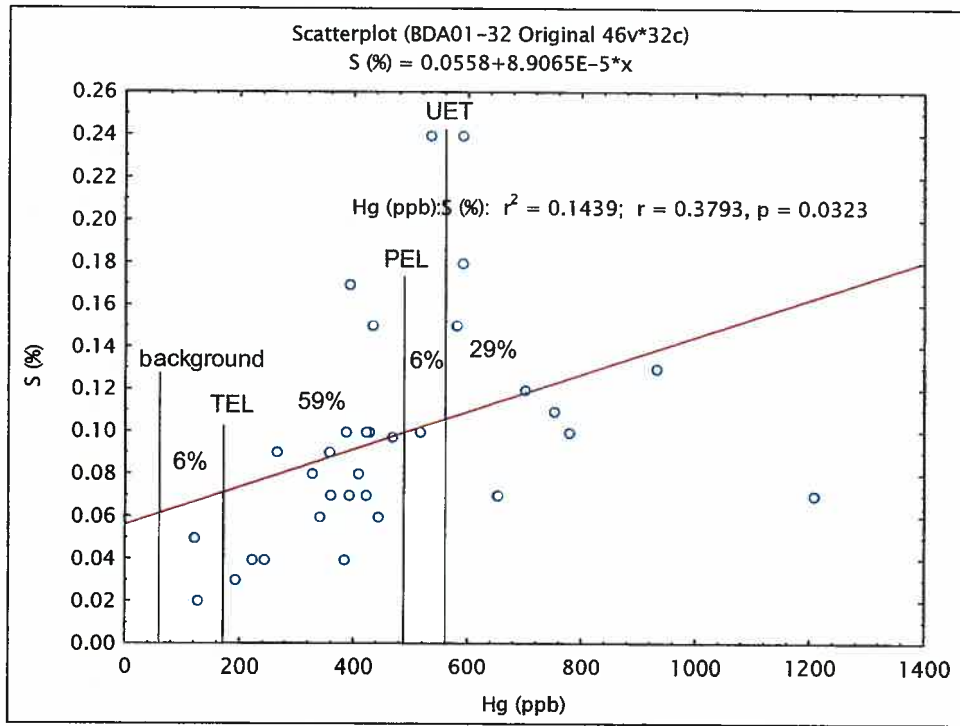
- LTEL; Lowest ARCs H. azteca Threshold Effects Level
- TEL: Threshold Effects Level
- PEL: Probable Effects Level
- UET: Upper Effects Threshold



Higher Risk

after NOAA(1999)







Various Criteria for Sediment Contamination

PTEs	NOAA SquiRTs for Freshwater Sediment*					Netherlands**			Japan
	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	

(Unit: mg/kg)

## [ Toxicity of Mercury ]

- Mercury
  - Metal mercury           Hg<sup>0</sup>
  - Inorganic mercury ion   Hg<sup>+</sup>, Hg<sup>2+</sup>
  - Organic mercury        R-Hg
    - CH<sub>3</sub>-Hg<sup>+</sup>
    - C<sub>6</sub>H<sub>5</sub>-OCOCH<sub>3</sub>
- R-Hg >> Hg<sup>2+</sup> >> Hg<sup>0</sup>