

US EPA ARCHIVE DOCUMENT



Hydrocarbon and Ecotoxicity of Water and Sediment from Iguassu and Barigui Rivers after the Oil Spill occurred in July/2000, Parana, Brazil



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About the accident

- **On the 16th. of July, 2000**
- **4000 m³ crude oil spilled**
- **cause: pipeline rupture**



Iguassu River oil spill - July/2000

Site of the spill



Paraná



Iguassu River oil spill - July/2000

Parana - Iguassu River



o BOOMS



Iguassu River oil spill - July/2000

Iguassu River Ecosystem





Iguassu River oil spill - July/2000

Iguassu River - Booms at P6 - Balsa Nova





Monitoring Program - Sites of sampling

Water or Sediment	Codes	Station	North	East	Region
UPSTREAM SITES					
W, S	M Bar	Barigui river – Upstream (3.5 km)	7172504	666565	Bridge near pulp industry.
W, S	M Igu	Iguassu River – Upstream	7162964	664537	Bridge BR116
SPILL SITES					
W, S	P0 av	Barigui river - Point 0 (2 km down spill)	7169315	665208	Arroio Saldanha and Barigui river confluency
W, S	P1	Barigui river - Point 1	7168480	665877	Booms at P1
W, S	P2	Barigui river - Point 2	7166053	664977	Cachimba bridge
DOWNSTREAM SITES IN IGUASSU RIVER					
W, S	P3	Point 3 (7 km down spill)	7169000	655550	Iguassu river
W, S	P4	Point 4 (17 km down spill)	7167712	649259	Guajuvira (bridge)
W, S	P5	Point 5 – (28 km down spill)	7167550	644050	General Lucio
W, S	P6	Point 6 – (44 km down spill)	7167792	637458	Balsa Nova
W, S	P6A	Point 6 A (approx 48 km)	7168539	636259	Balsa Nova
W, S	P7	Point 7 - (84 km down spill)	7174136	611931	Porto Amazonas – (bridge)
W, S	P8	Point 8 - (174 km down spill)	7137827	561614	Sao Mateus do Sul (bridge)
W, S	P9	Point 9 – (314 km down spill)	7097603	495168	Uniao da Vitoria (intake station to drinking)



Iguassu River oil spill - July/2000

**P 0 - Terrestrial Area
(P0 adj)**



Spilled Oil Characterization

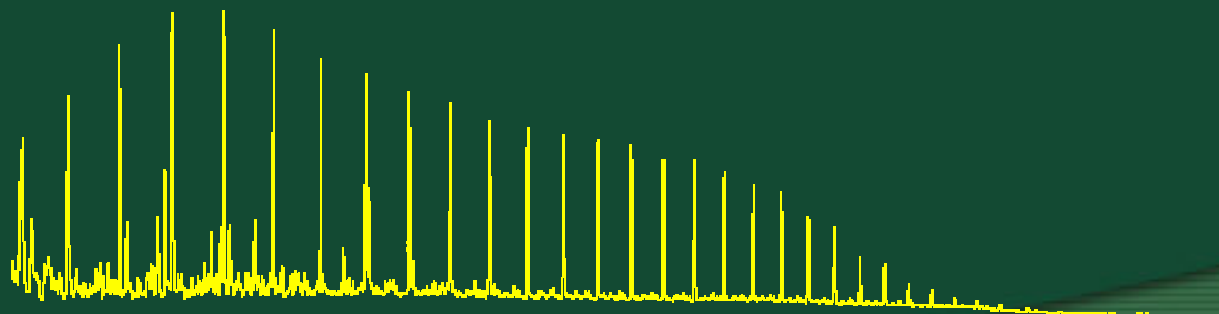
°API: 41 Density 20/4°C: 0,8164

SIM DIS: <36 to 588°C (residue 27% up to 588°C)

Evaporation estimative: 26% (up to 180°C)

SARA (% weight): S= 71.3 A=18.2 R=9.6 A=0.8

PAH: 16 mg/g (mainly naphtalenes, phenantrenes)



Toxicity of the Spilled Oil

Spilled Oil	<i>Vibrio fischeri</i> (Microtox)	<i>Daphnia similis</i>	<i>Brachydanio rerio</i>
(Code 1447)	CE50_{15min} (% WSF)	CE50_{48h} (% WSF)	CL50_{48h} (% WSF)
Test 1	7,13	-	28,15
Test 2	8,31	23,96	-
Test 3	7,69	49,52	-



Water Analysis during 3 months (Jul to Aug/2000)

- **360 Chemical Analysis in 120 samples**

TPH (GC/FID)

Biomarkers (GC/MS)

BTEX (P&T/GC/PID)

Phenols (GC/MS)

PAH (UV-Fluorescence and GC/MS)

- **Metals and Pesticides in 14 samples**

- **186 toxicity tests in 44 samples**

Vibrio fisheri

Daphnia similis

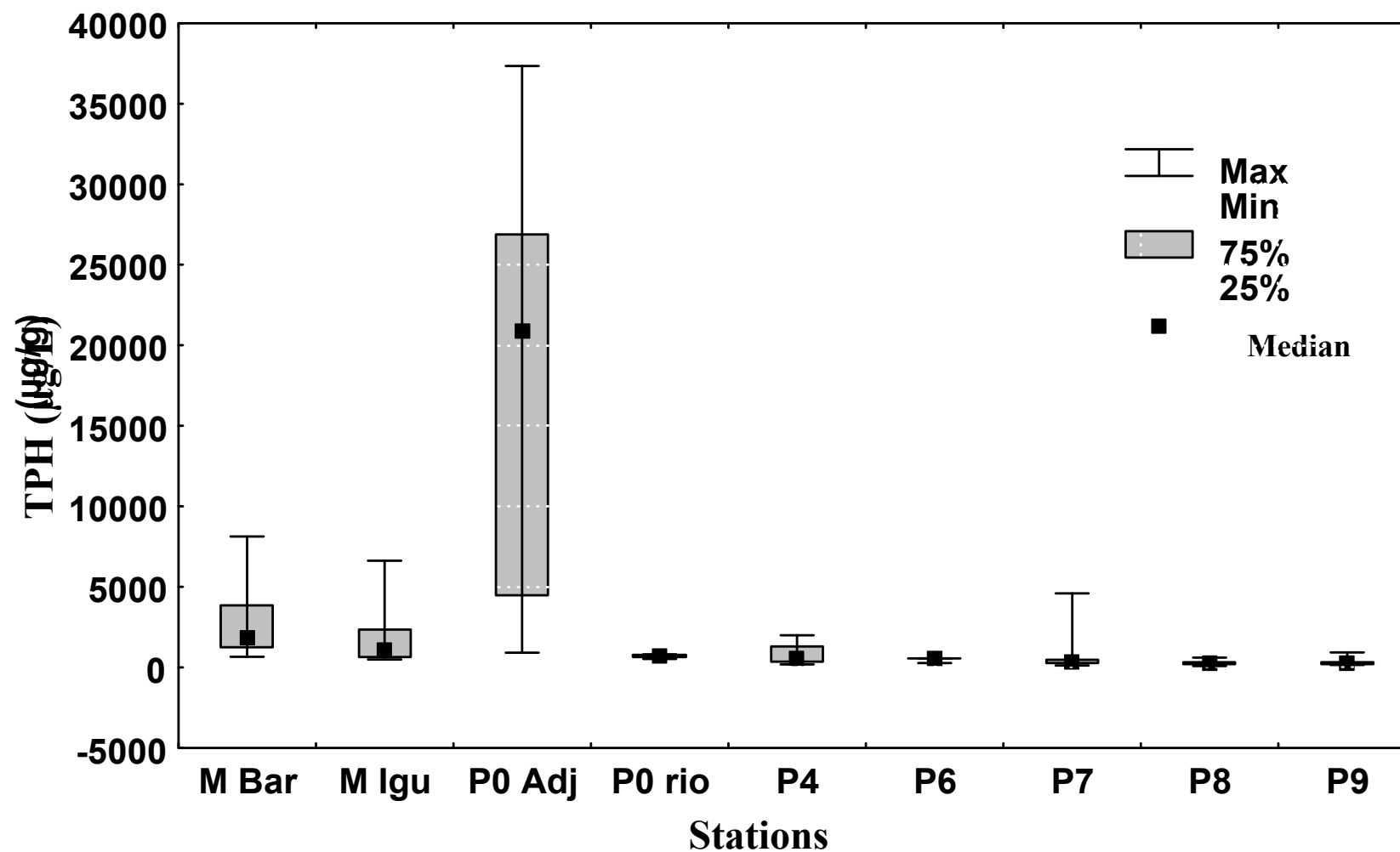
Brachydanio rerio

Ceriodaphnia dubia



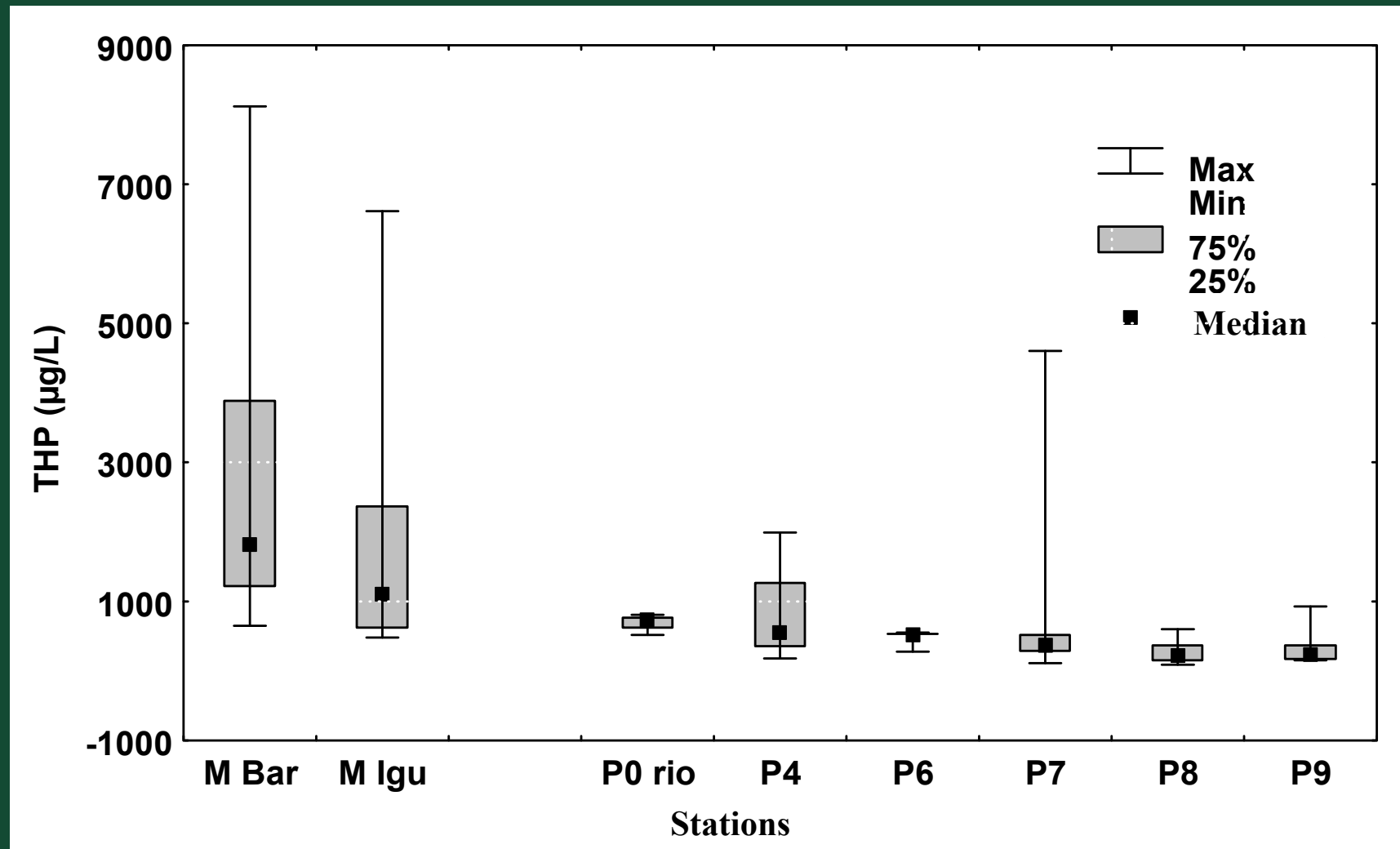


TPH in the Rivers Waters





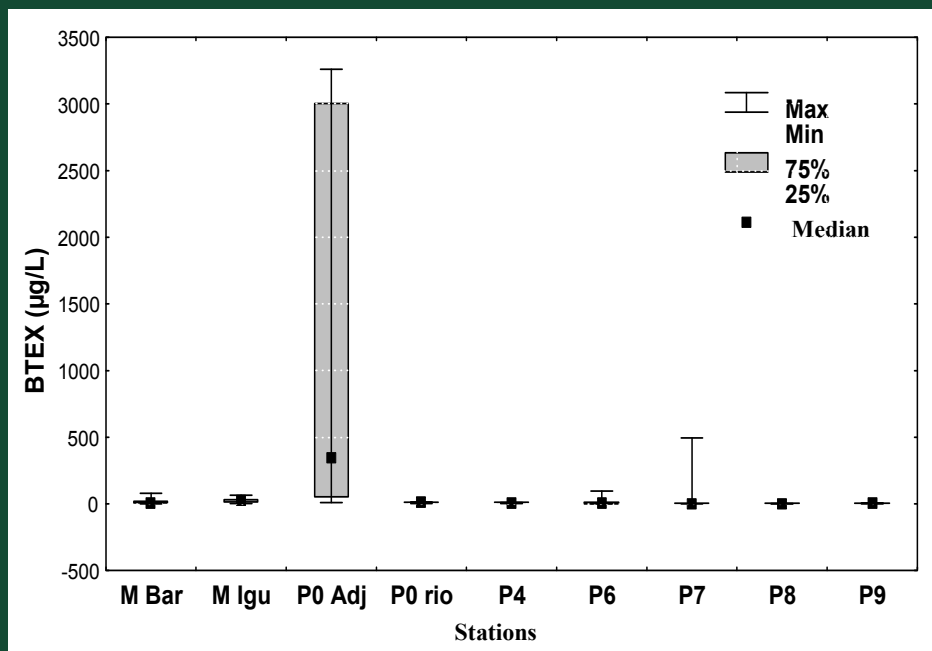
TPH in the Rivers Waters (excluding P 0 terrestrial area)



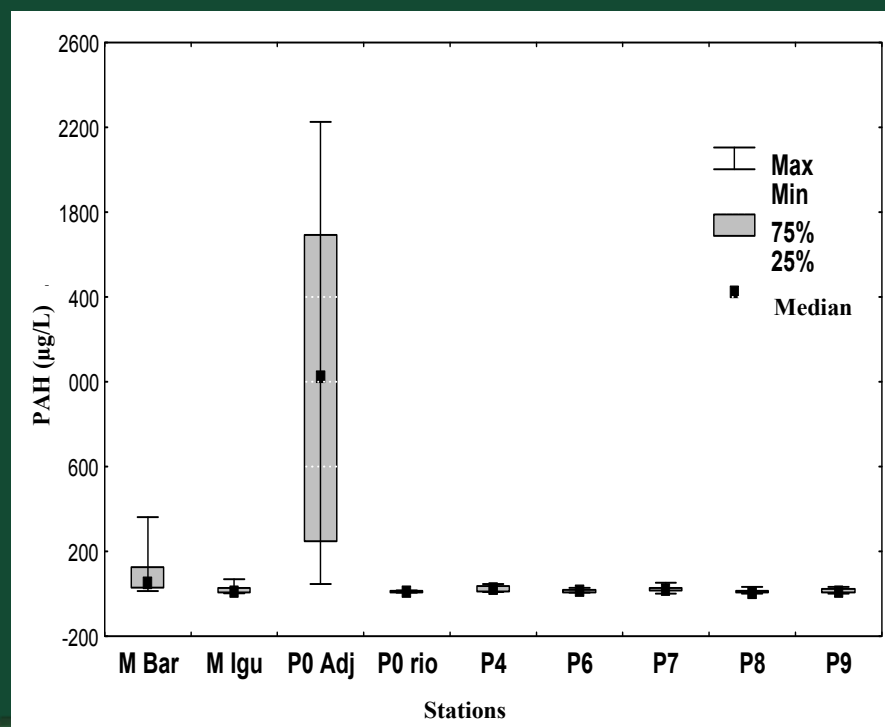


BTEX and PAH in the Rivers Waters

BTEX



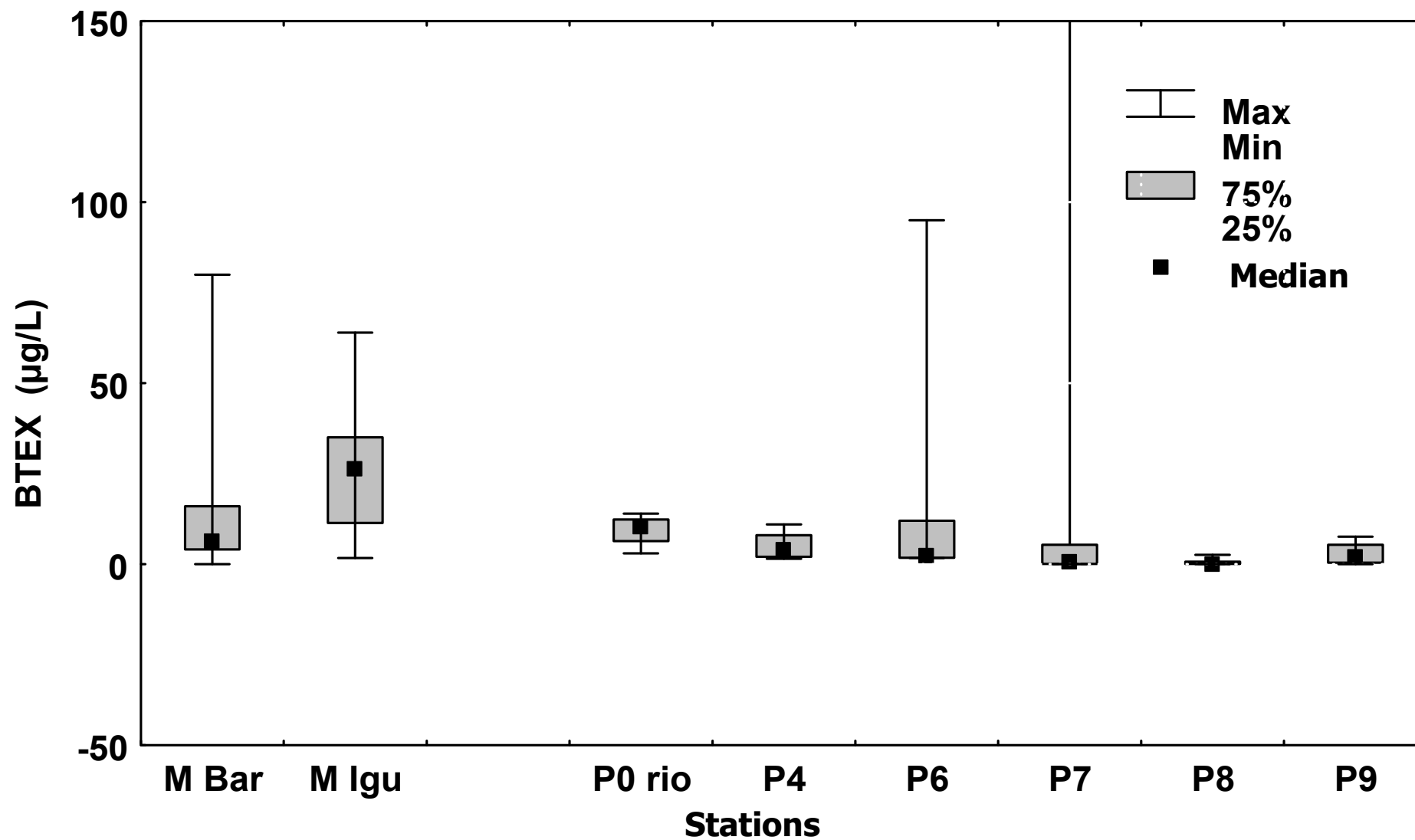
PAH (UV-Fluorescence)





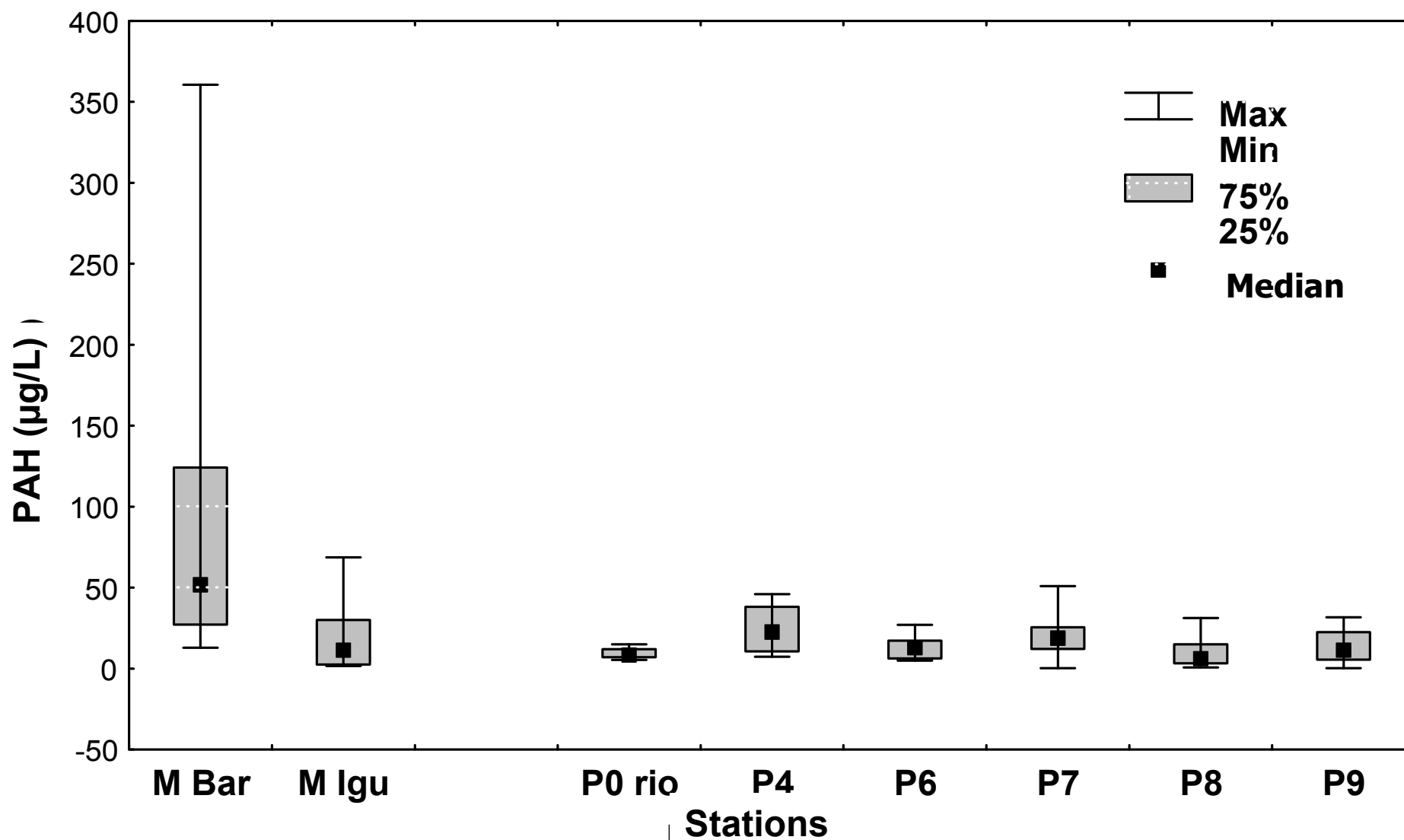
Iguassu River oil spill - July/2000

BTEX in the Rivers Waters (excluding P 0)





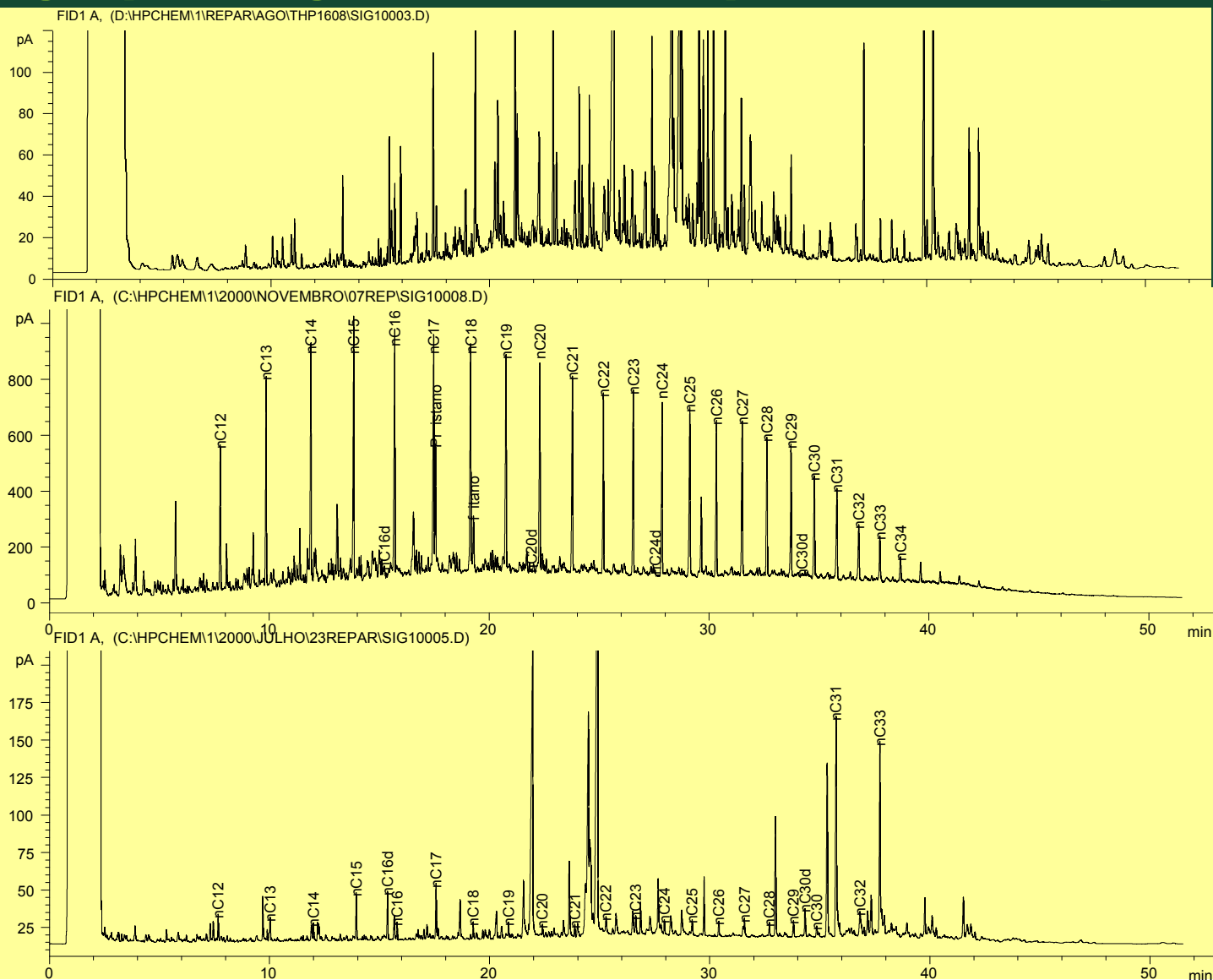
PAH in the Rivers Waters (excluding P 0)





Iguassu River oil spill - July/2000

Fingerprinting of Water Samples Extracts (TPH GC-FID)



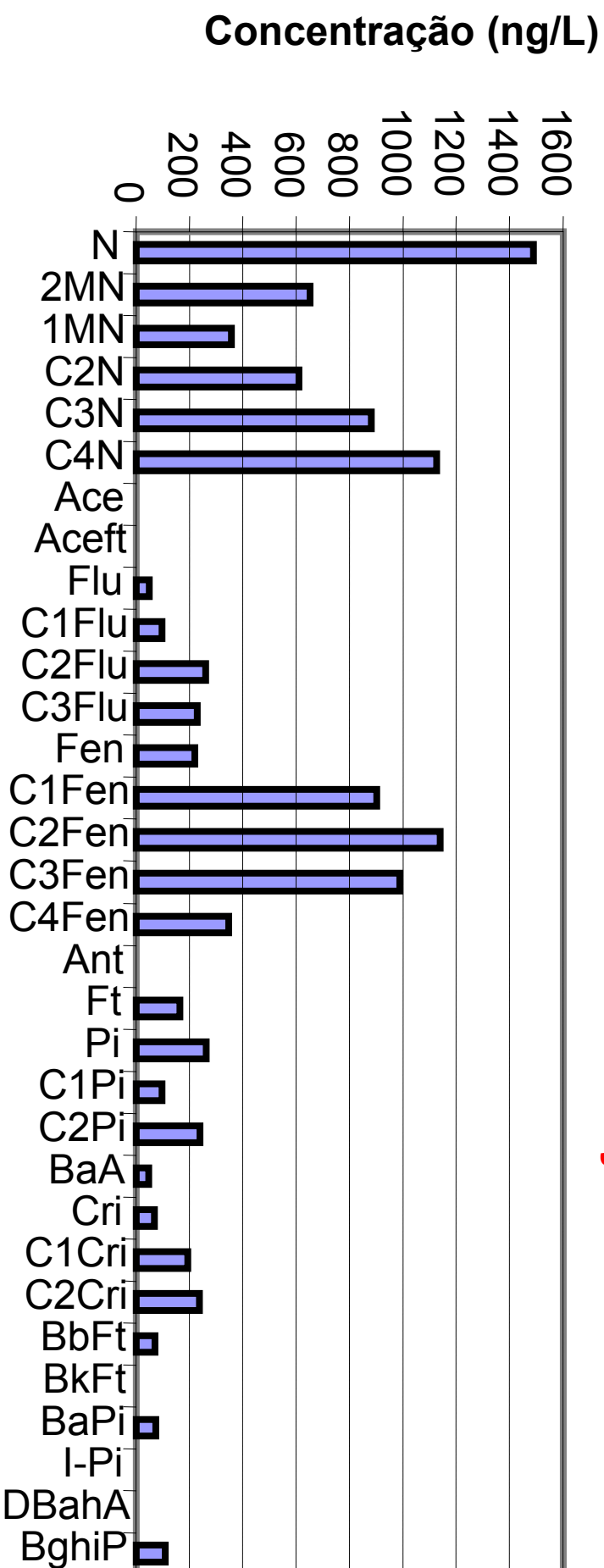
Barigui River
Upstream
15/Aug/00

P0 Terrestrial
area
04/Oct/00

P6 Guajuvira
20/Jul/00

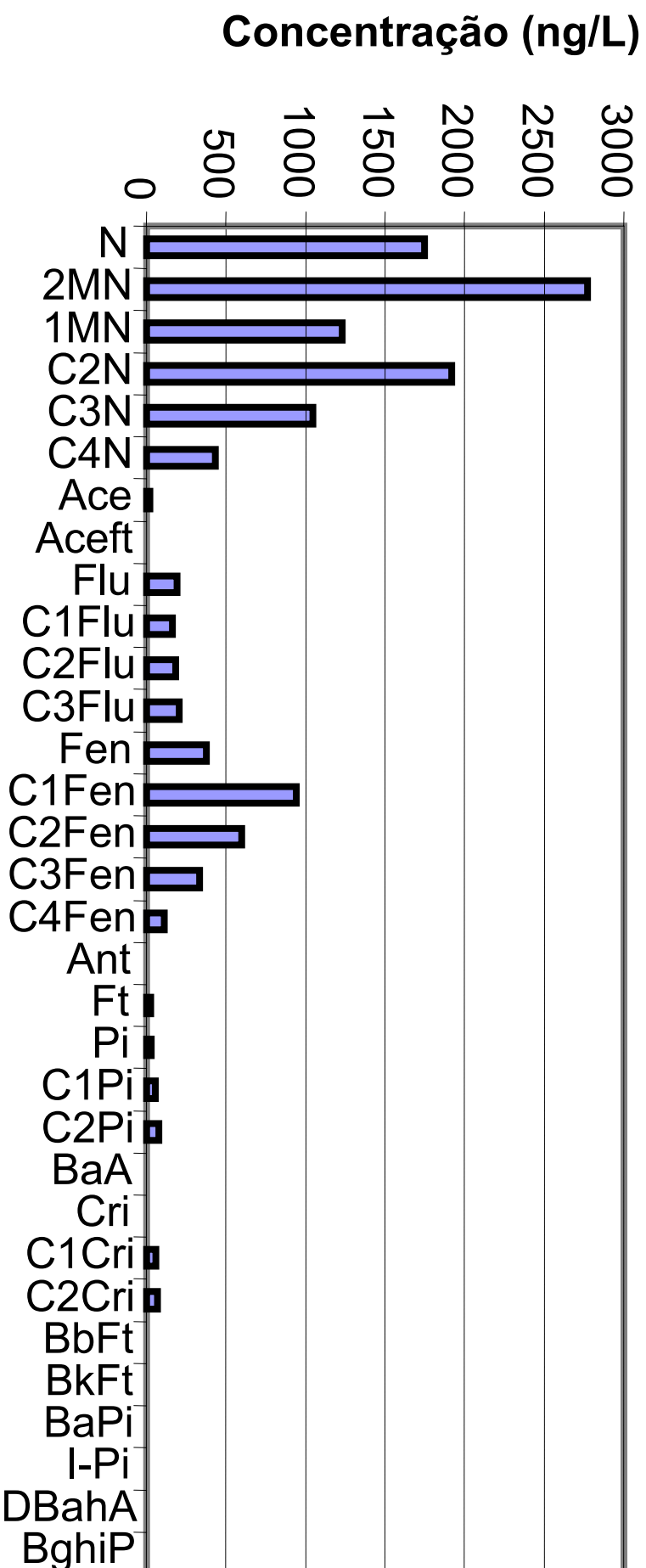
PAH by GC-MS in rivers water

UPSTREAM BARIGUI RIVER 20/July/2000



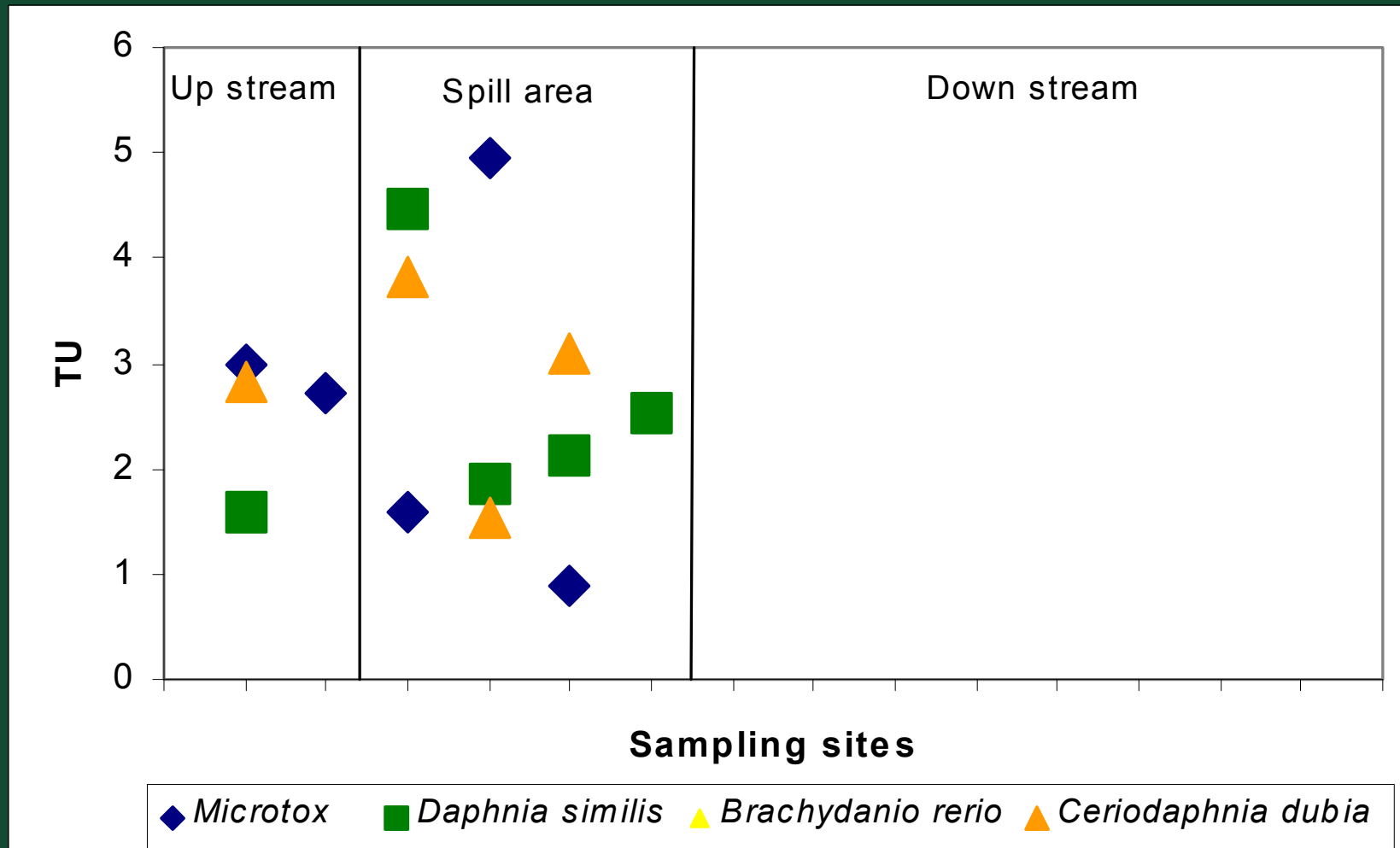
PAH by GC-MS in rivers water

P4 Guajuvira 20/July/2000





TOXICITY IN RIVERS WATER



TU= Toxic Units (express the toxicity as a inverse of CL50)

Water Toxicity

- The toxicity tests indicated the impact was restrict to P0 terrestrial area;
- it was observed toxicity in other parts of the rivers not related to the oil spill (caused by other sources)

Vibrio fischeri
Daphnia similis
Brachydanio rerio
Ceriodaphnia dubia





CONCLUSIONS ABOUT RIVER WATER

- ⇒ **No contamination was observed at Iguassu river at P7 (84 km), P8 (174 km), P9 (314km) stations during the monitoring after the spill;**
- ⇒ **The BTEX, TPH, PAH results indicated:**
 - **the high concentrations were obtained at P0 terrestrial region;**
 - **the upstream stations demonstrated high level of hydrocarbon;**
 - **the downstream stations at Barigui and Iguassu rivers showed background hydrocarbon levels after 1 week of the accident;**
- **No match with the Biomarkers of the spilled oil was observed for the downstream stations even in Barigui or Iguassu river.**

14 Sediment Samples (1 month after spill)

Chemical Analysis

TPH (GC/FID)

BTEX (P&T/GC/PID)

PAH (GC/MS)

Metals

n-Alkanes (GC/FID)

UCM (GC/FID)

Phenols (GC/MS)

Pesticides

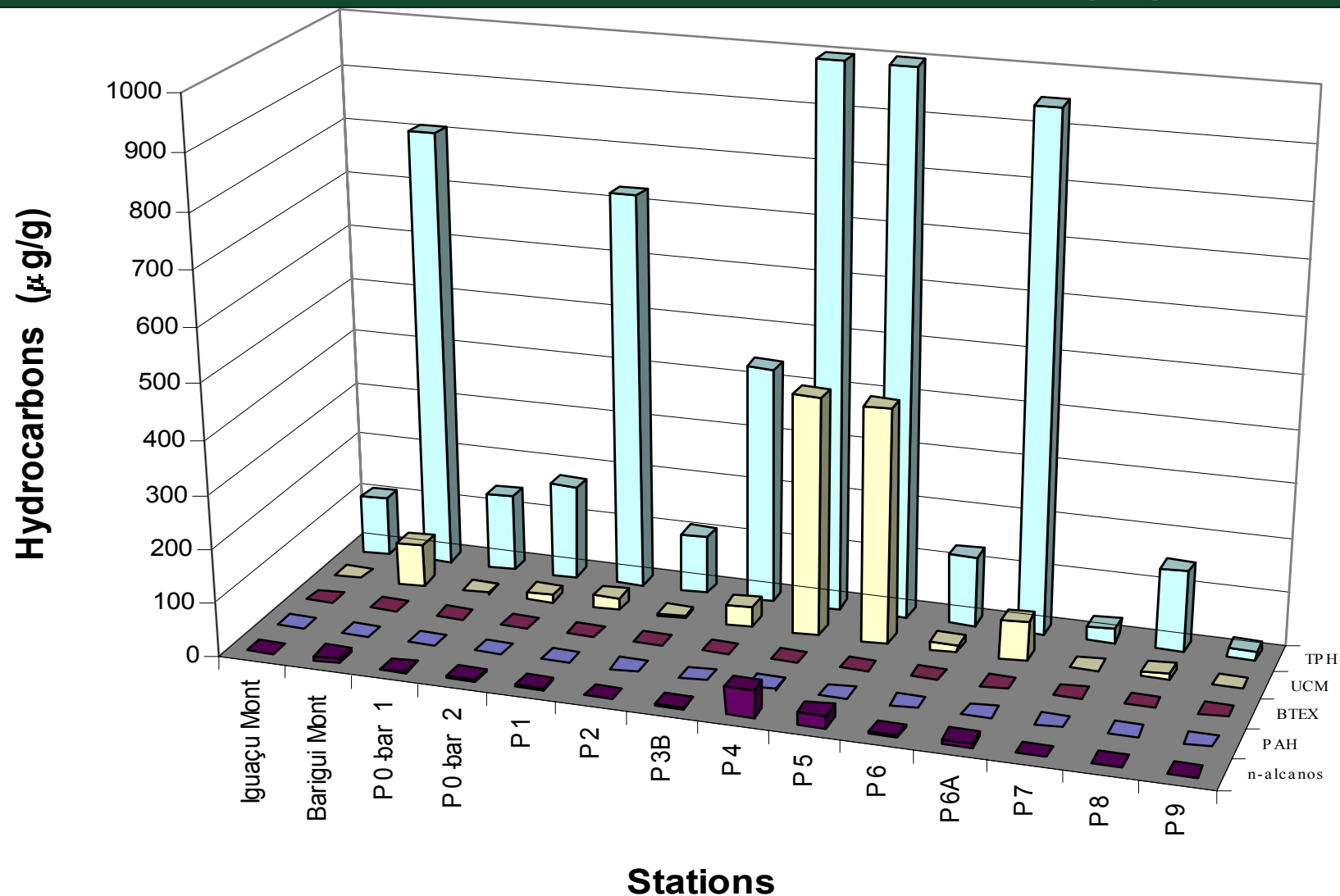
Toxicological assays

(Microtox and *Daphnia similis*)



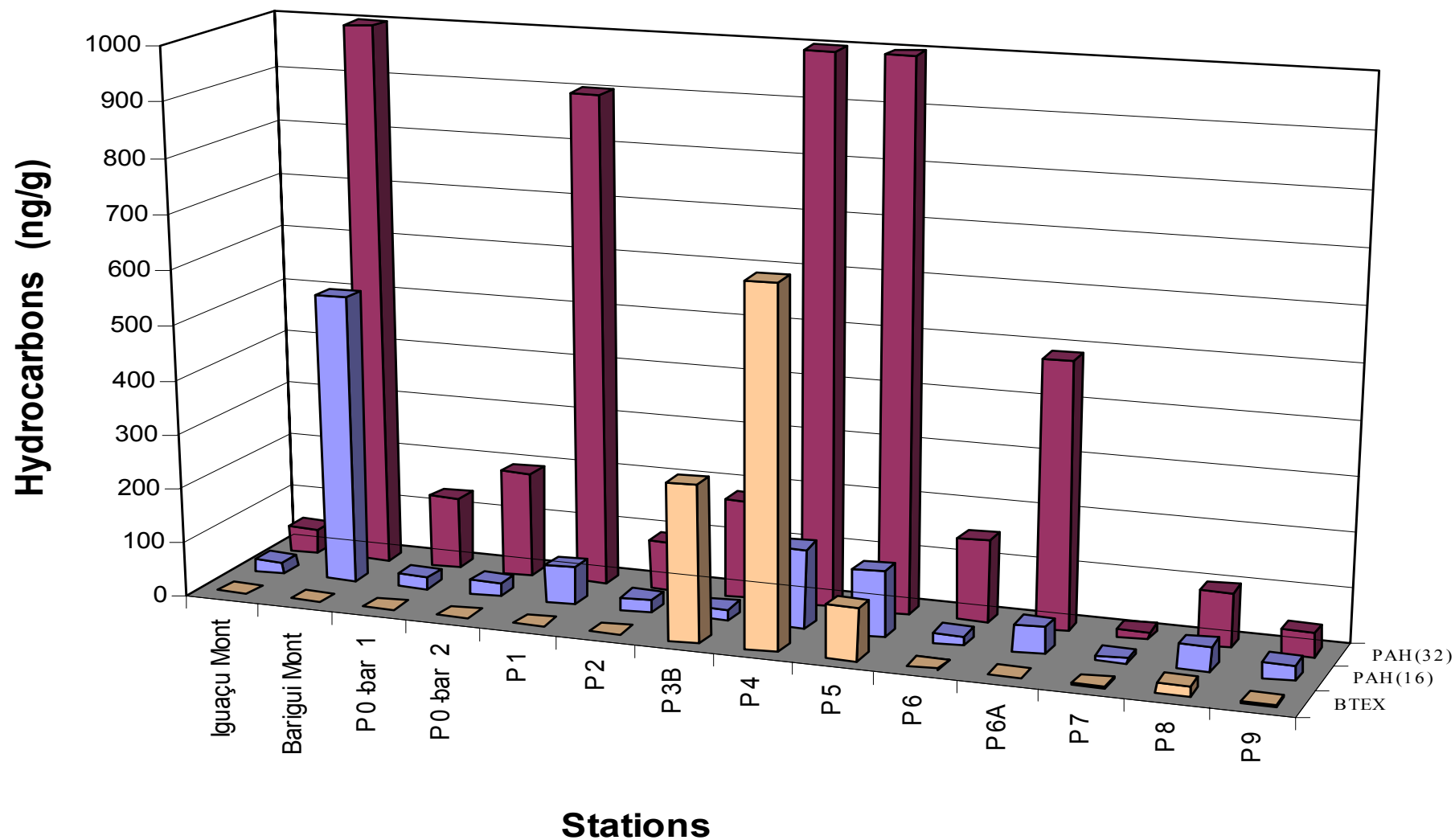


Hydrocarbons in River Sediments - $\mu\text{g/g}$ (ppm)





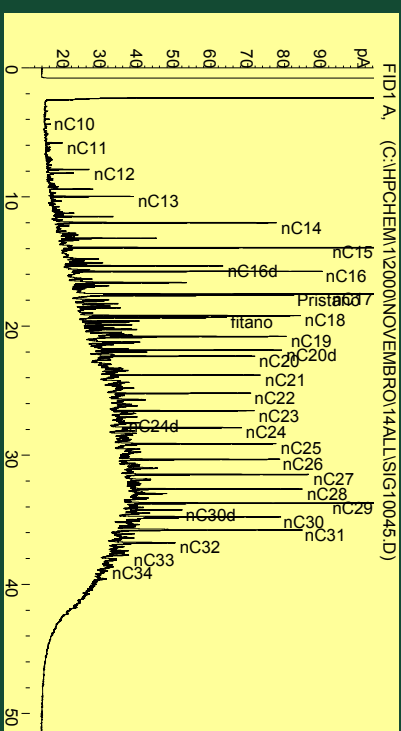
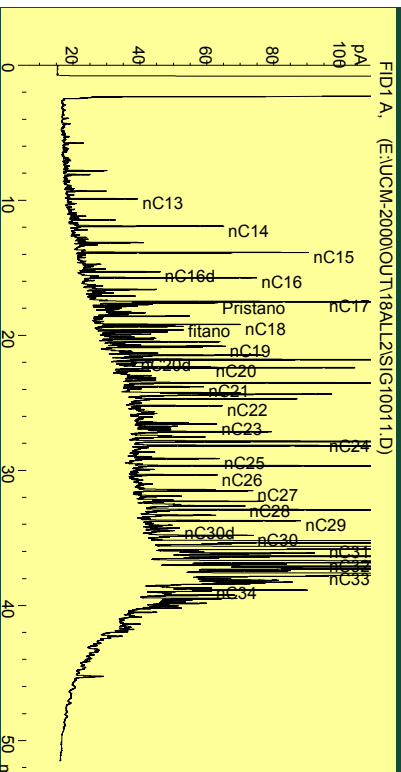
Hydrocarbons in River Sediments - ng/g (ppb)



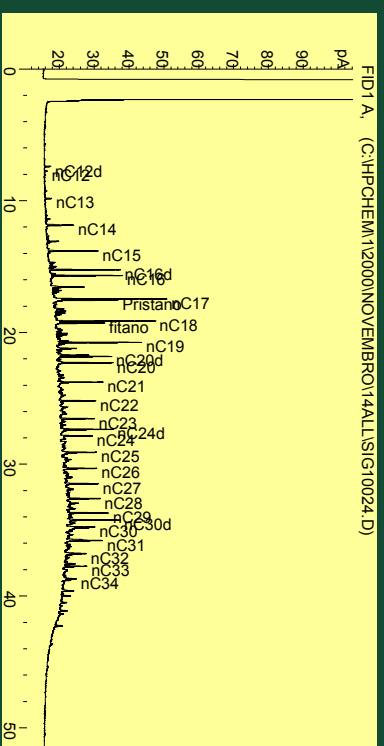
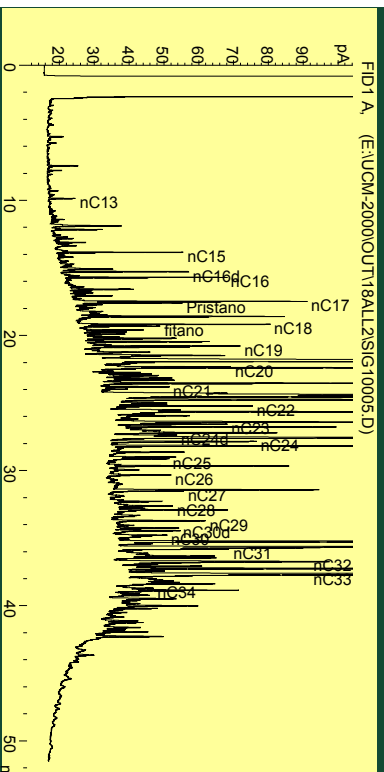


Iguassu River oil spill - July/2000

Fingerprinting of Sediment extracts (GC-FID)



P4 - Guajuvira
22/Aug/00



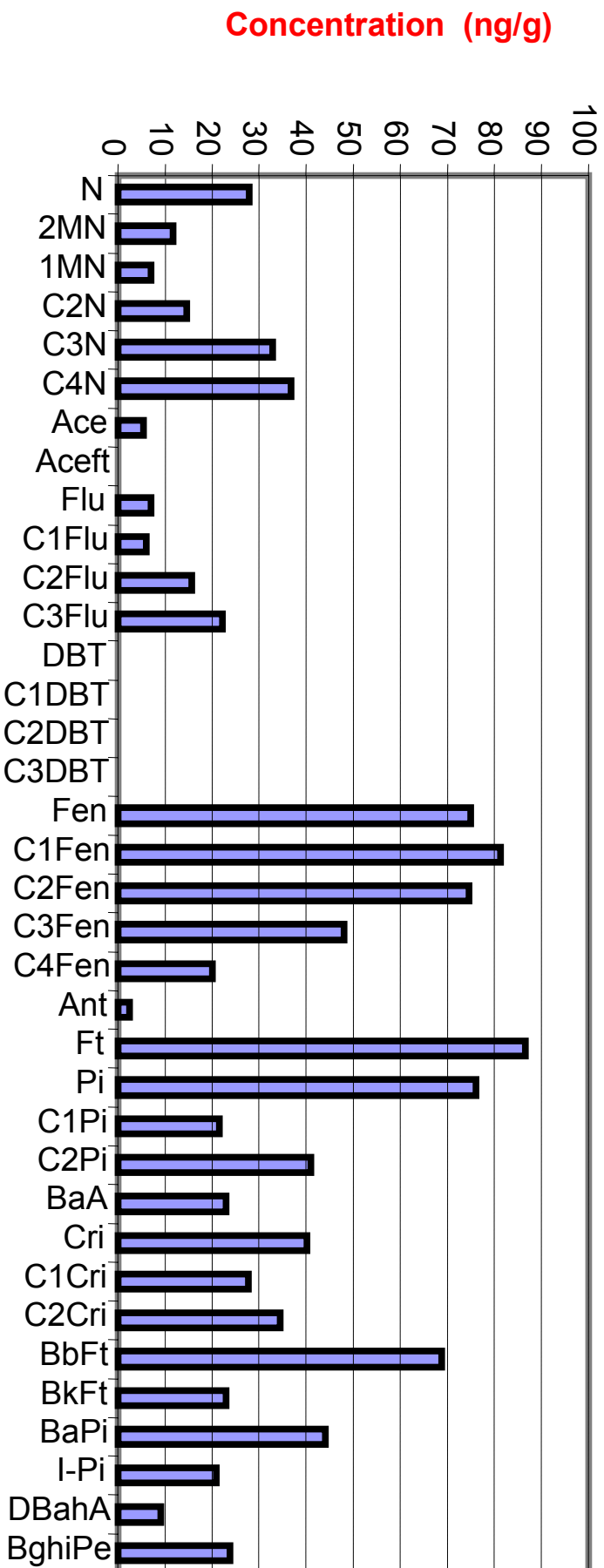
Barigui River
upstream
24/Aug/00

Total extract (TEM)

n-alkanes (after cleanup)

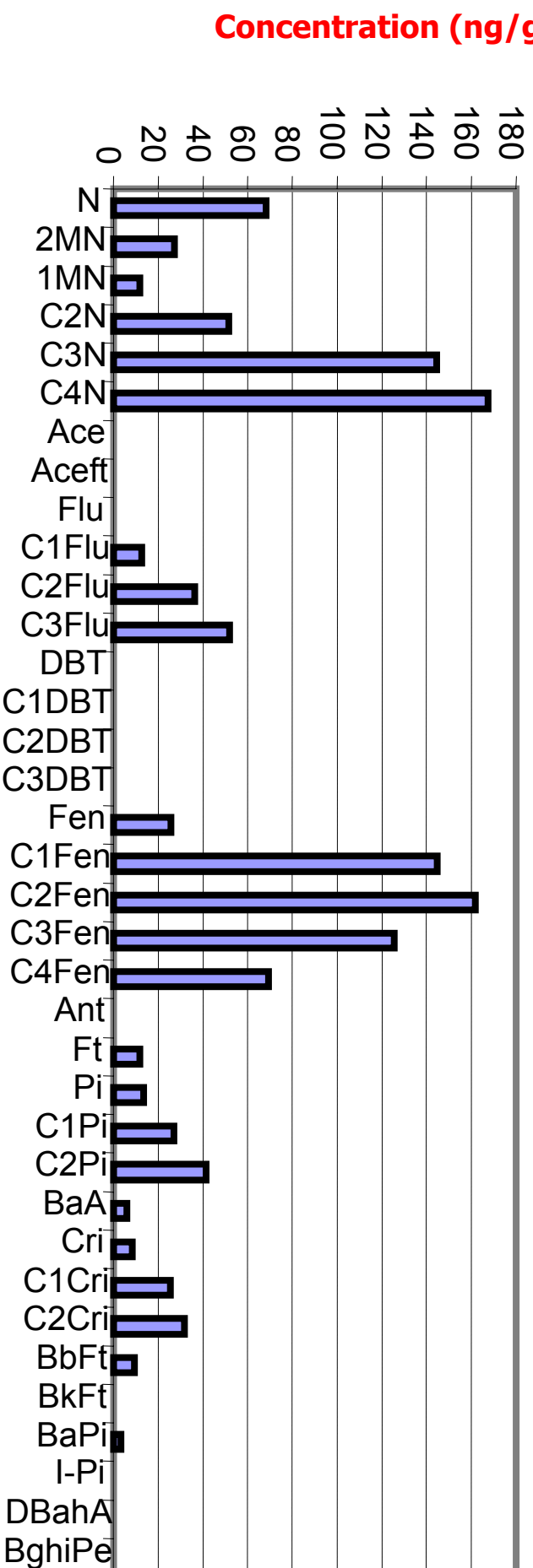
PAH in sediment by GC-MS

UPSTREAM BARIGUI RIVER



PAH in sediment by GC-MS

Station P4- Guajuvira





PAHs in Sediments - Literature Comparison

Iguassu and Barigui Rivers:

Upstream: 47 - 1028 $\mu\text{g/kg}$

Spill Area: 89 - 901 $\mu\text{g/kg}$

Downstream: 13 to 1590 $\mu\text{g/kg}$

GC-MS
(sum 36 PAH)

Other brazilian rivers:

Tapajos River: 21 - 2032 $\mu\text{g/kg}$

Guandu River: 662 - 8091 $\mu\text{g/kg}$

Solimoes River: 251 - 1600 $\mu\text{g/kg}$

HPLC - UV
only the 16 PAH



Toxicity of the sediments leaching

SAMPLES	Microtox (<i>Vibrio fischeri</i>)	<i>Daphnia similis</i>
	CE50 _{5min} (%)	CE50 _{48h} (%)
Barigui River - UPSTREAM	NT	IT
Iguassu River UPSTREAM	NT	NT
P 0 Booms 1	IT	21,43
P 0 Booms 2	IT	IT
P1 - Barigui River	IT	100
P2 - Barigui River	NT	IT
P3 - Iguassu River	NT	NT
P4 - Iguassu River	NT	NT
P5 ---Iguassu River	IT	IT
P6 - Iguassu River	IT	10,00
P6A - Iguassu River	IT	22,36
P7- - Iguassu River	NT	70,71
P8 - - Iguassu River	IT	< 10,00
P9 - - Iguassu River	IT	10,00

NT – non toxic

IT – incipient toxicity



CONCLUSIONS About the River Sediments

UPSTREAM:

- The background levels at the upstream stations from Barigui and Iguassu rivers showed high level of contamination (metals and hydrocarbons);
- Barigui river more contaminated than Iguassu river.

DOWNSTREAM:

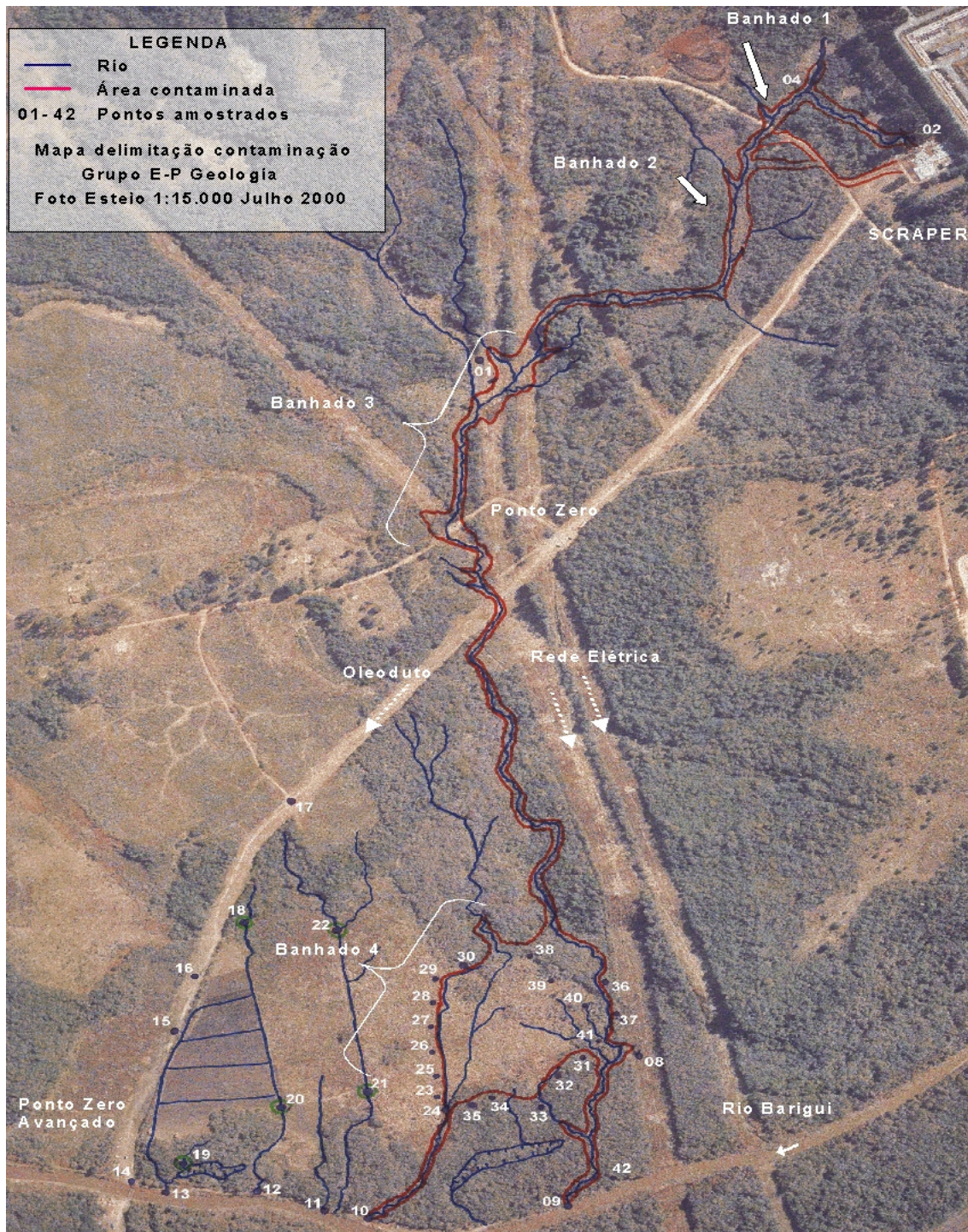
- The sites more contaminated (P4 and P5) suggested some oil presence but the biomarkers (terpanes and steranes) analysis showed no matches with the spilled oil ;
- Literature comparison of PAH in sediments showed similar concentration levels for other Brazilian rivers;
- High level of toxicity was observed to stations situated far from the spill site suggesting other sources of pollutants.



GENERAL CONCLUSION

About the Rivers

- **It was not observed significant contamination in water or sediments from Barigui and Iguassu rivers after the cleanup step;**
- **Same level of hydrocarbon in upstream or downstream the accident (exception P4 and P5);**
- **Literature comparison of Hydrocarbon in sediments showed similar concentration levels for other Brazilian rivers;**
- **High level of toxicity was observed to stations situated far from the spill site suggesting other sources of pollutants.**



Iguassu River oil spill - July/2000

P 0 - Terrestrial Area
(P0 adj)

Groundwater
90 monitoring wells
(piezometers)

Soil
monitoring of approx. 80 sites



GENERAL CONCLUSIONS

About the terrestrial area

- The more contaminated site was the P0 terrestrial area (approx. 130,000 m²);
- The TPH, BTEX in groundwater revealed significant decrease in last campaign (Aug/2001);
- Several recovery and bioremediation methods have been implemented in this region;
- Long term soil and groundwater monitoring is still being conducted in this area.