



# 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 m<sup>3</sup> crude oil spilled
- cause: pipeline rupture



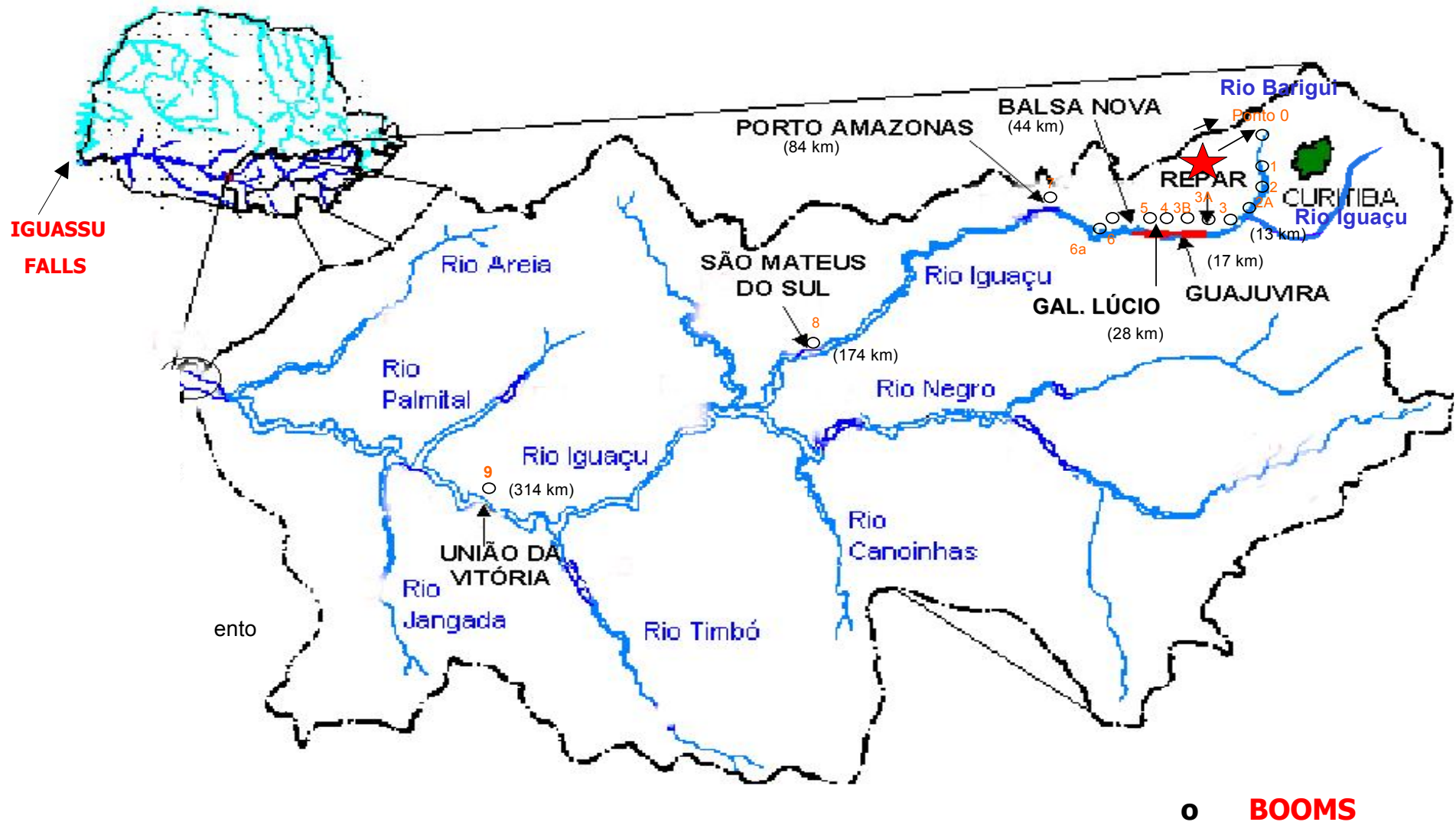
Site of the spill



Paraná



# Parana - Iguassu River







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
<b>UPSTREAM SITES</b>					
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
<b>SPILL SITES</b>					
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
<b>DOWNSTREAM SITES IN IGUASSU RIVER</b>					
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

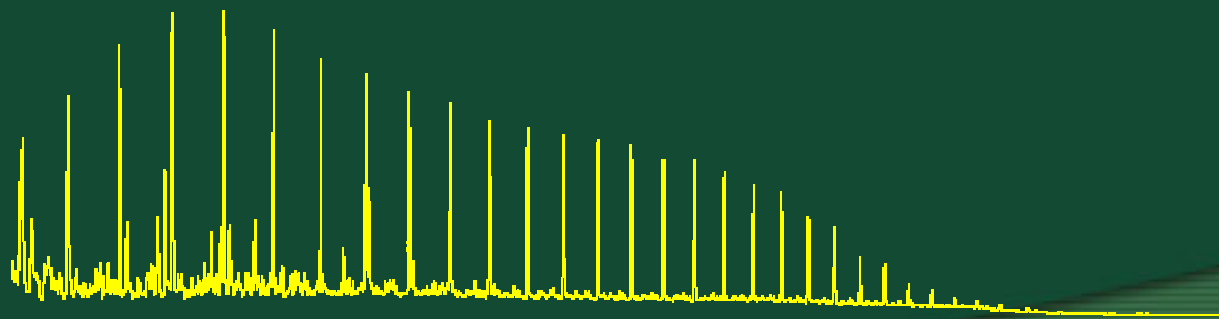
°API: 41      Density 20/4°C: 0,8164

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

<b>Spilled Oil</b>	<b><i>Vibrio fischeri</i></b> <b>(Microtox)</b>	<b><i>Daphnia similis</i></b>	<b><i>Brachydanio rerio</i></b>
(Code 1447)	<b>CE50<sub>15min</sub></b> <b>(% WSF)</b>	<b>CE50<sub>48h</sub></b> <b>(% WSF)</b>	<b>CL50<sub>48h</sub></b> <b>(% WSF)</b>
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*

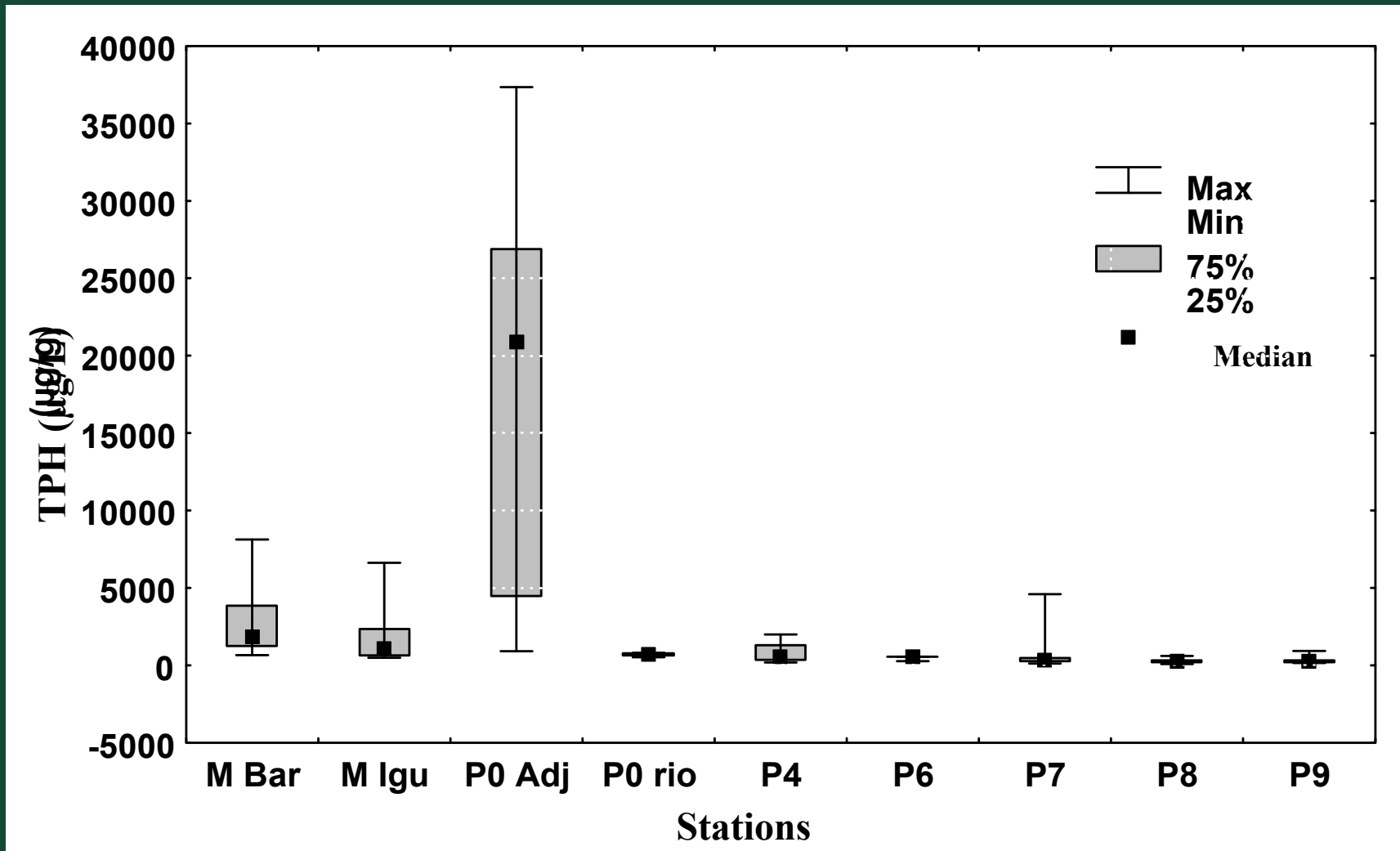
*Brachydanio rerio*

*Ceriodaphnia dubia*





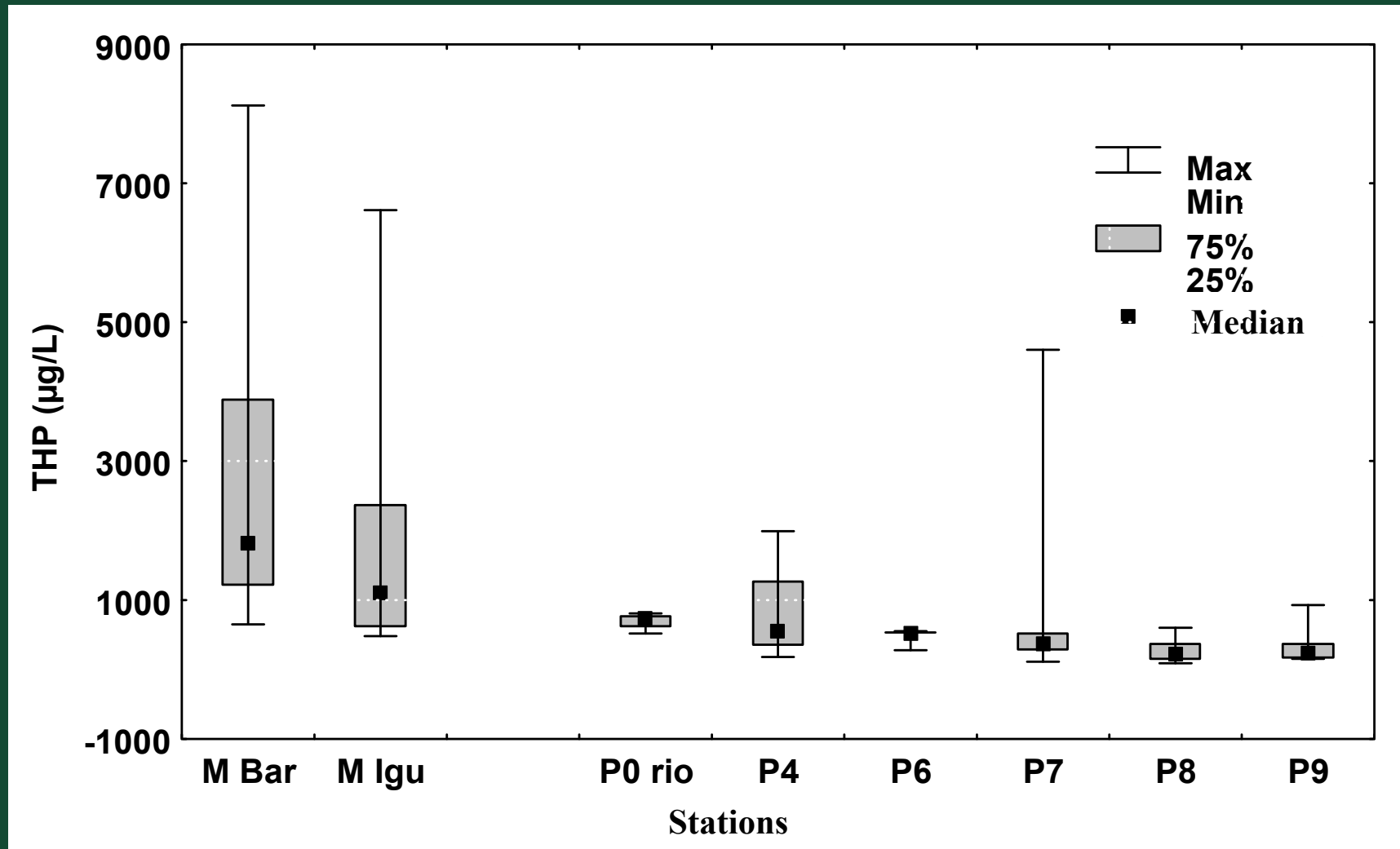
# TPH in the Rivers Waters







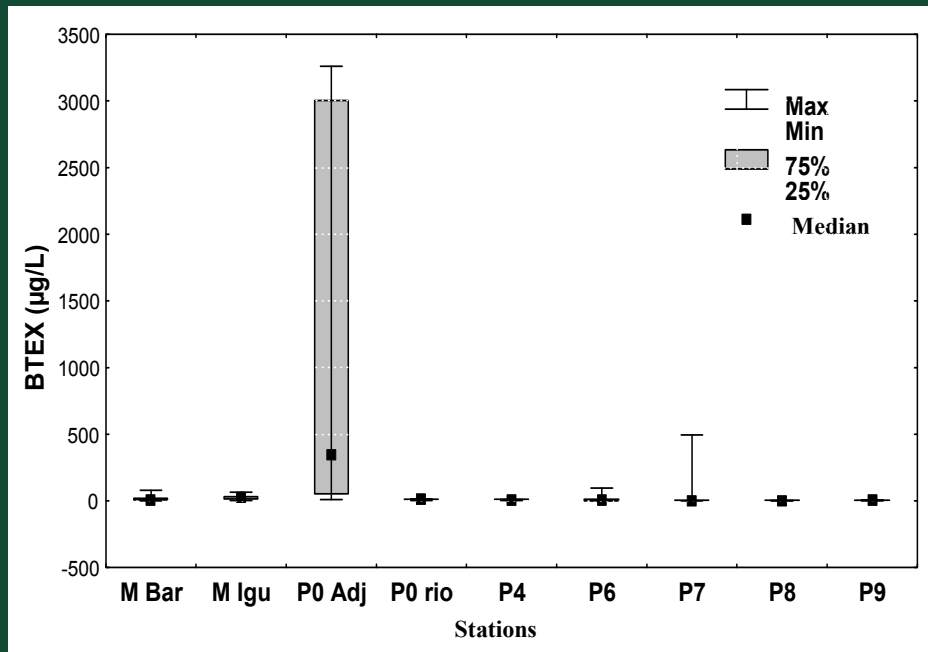
# TPH in the Rivers Waters (excluding P 0 terrestrial area)



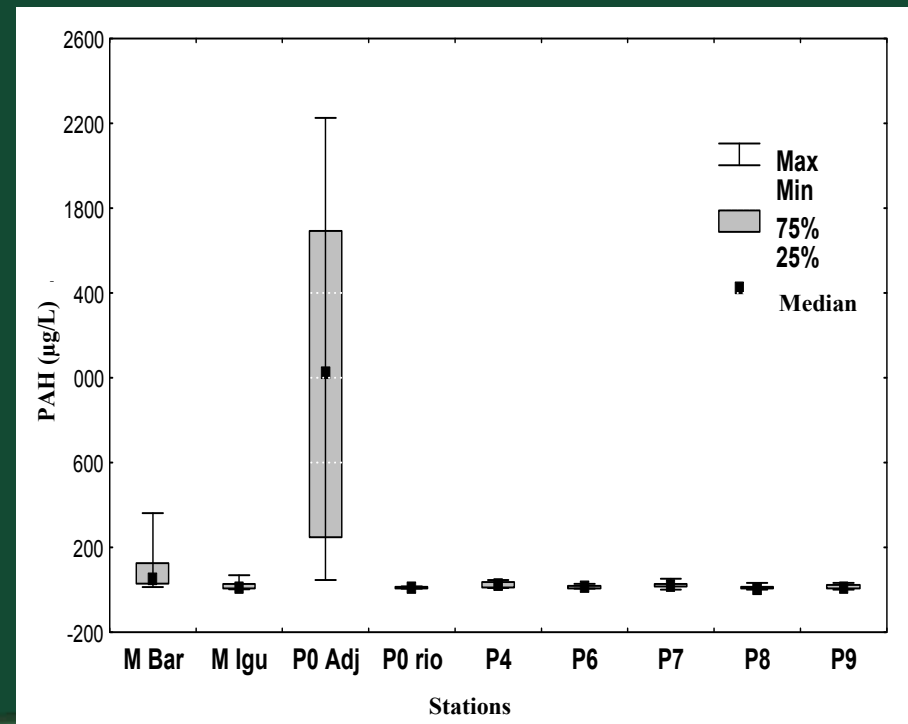


# BTEX and PAH in the Rivers Waters

## BTEX



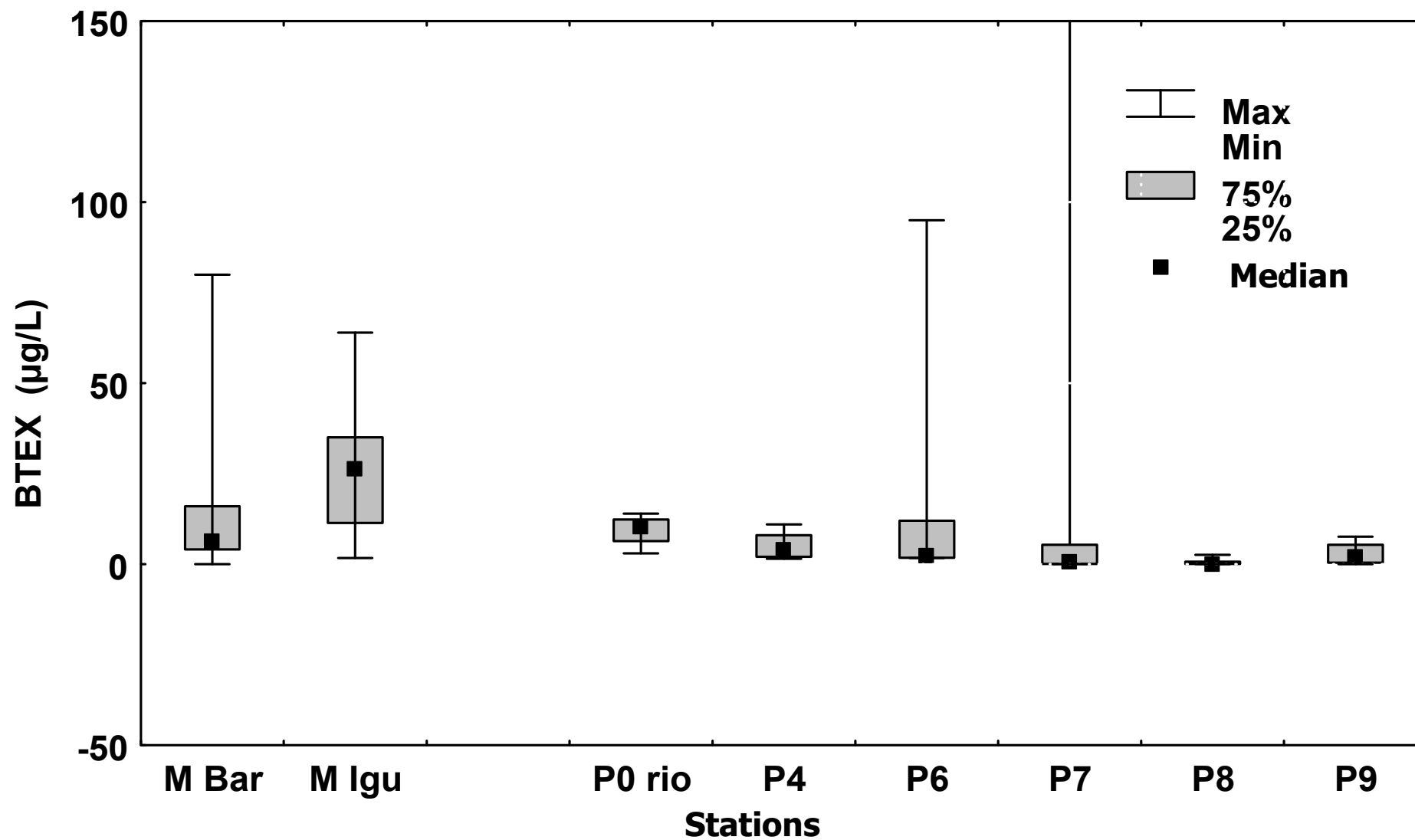
## PAH (UV-Fluorescence)





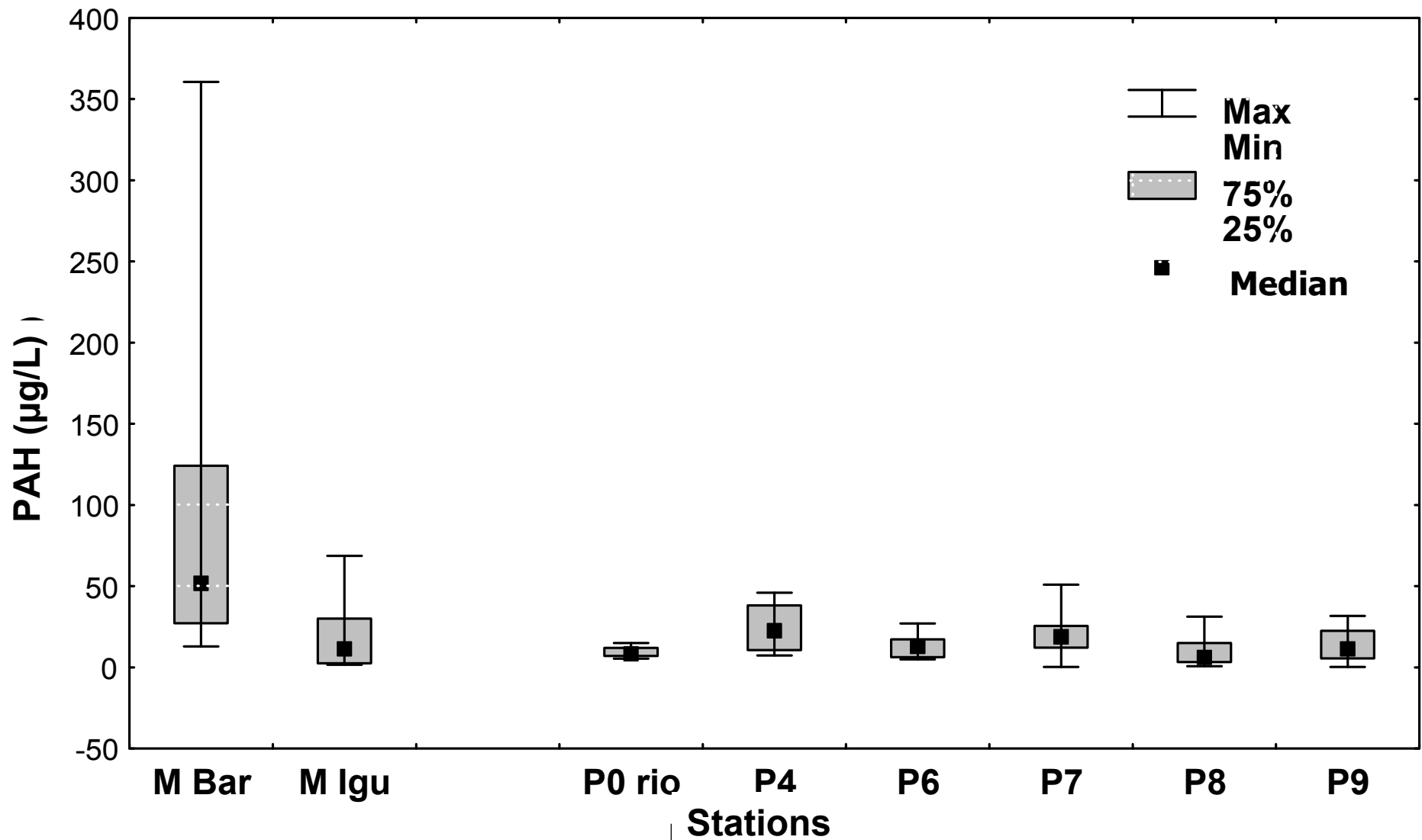


# BTEX in the Rivers Waters (excluding P 0)



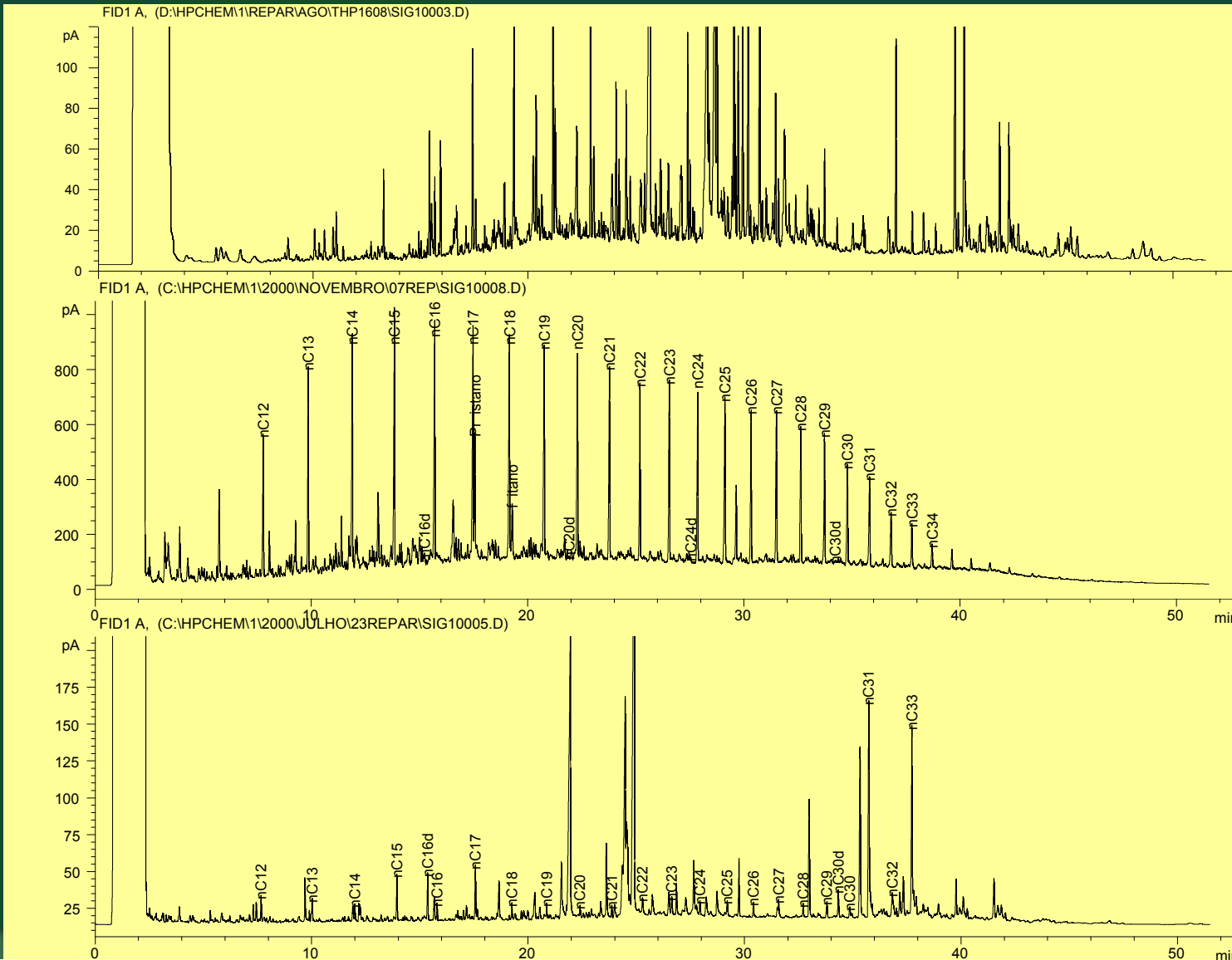


# PAH in the Rivers Waters (excluding P 0)





# Fingerprinting of Water Samples Extracts (TPH GC-FID)



**Barigui River  
Upstream  
15/Aug/00**

**P0 Terrestrial  
area  
04/Oct/00**

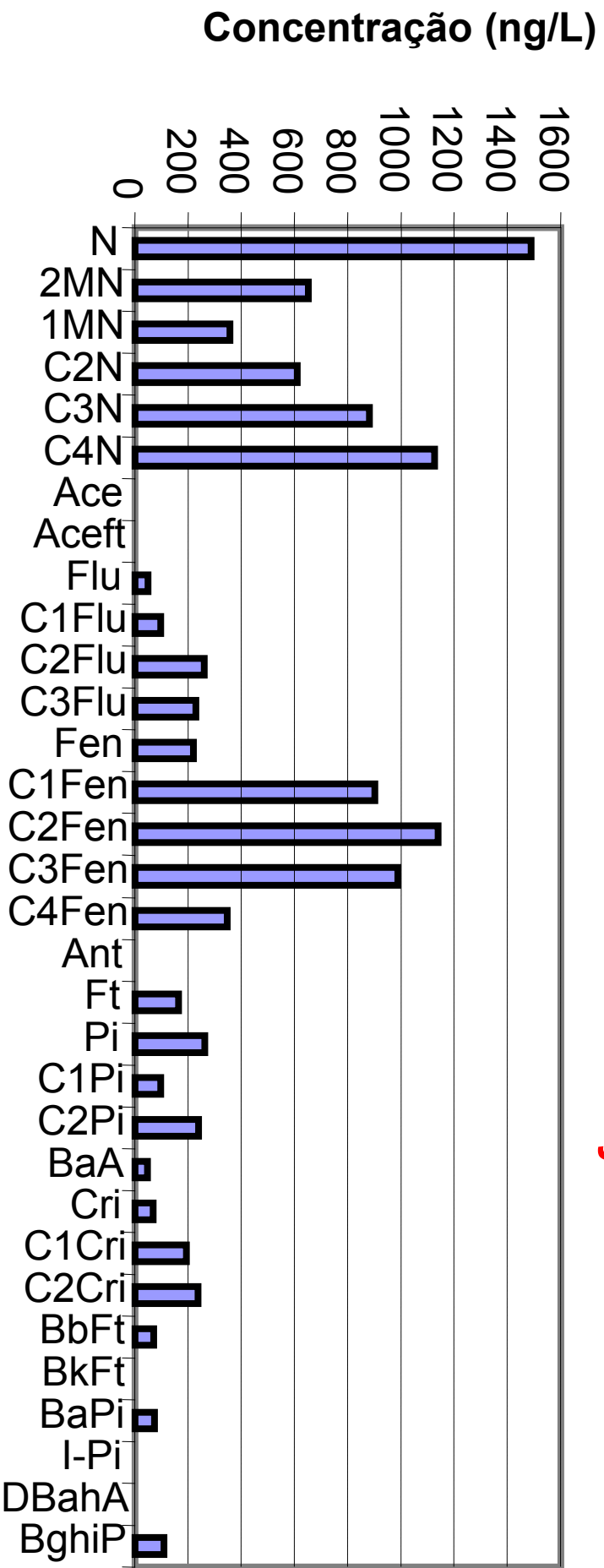
**P6 Guajuvira  
20/Jul/00**



Iguassu River oil spill - July/2000

# PAH by GC-MS in rivers water

UPSTREAM BARIGUI RIVER 20/July/2000



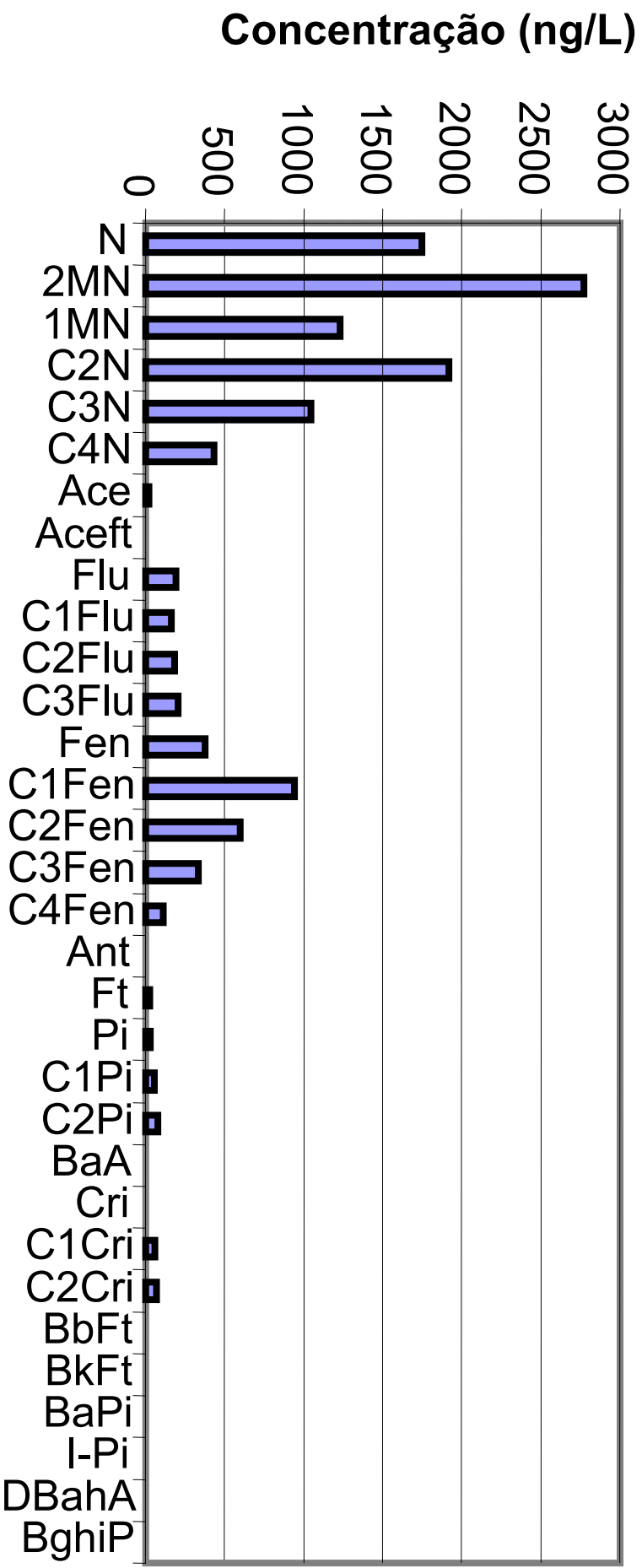




Iguassu River oil spill - July/2000

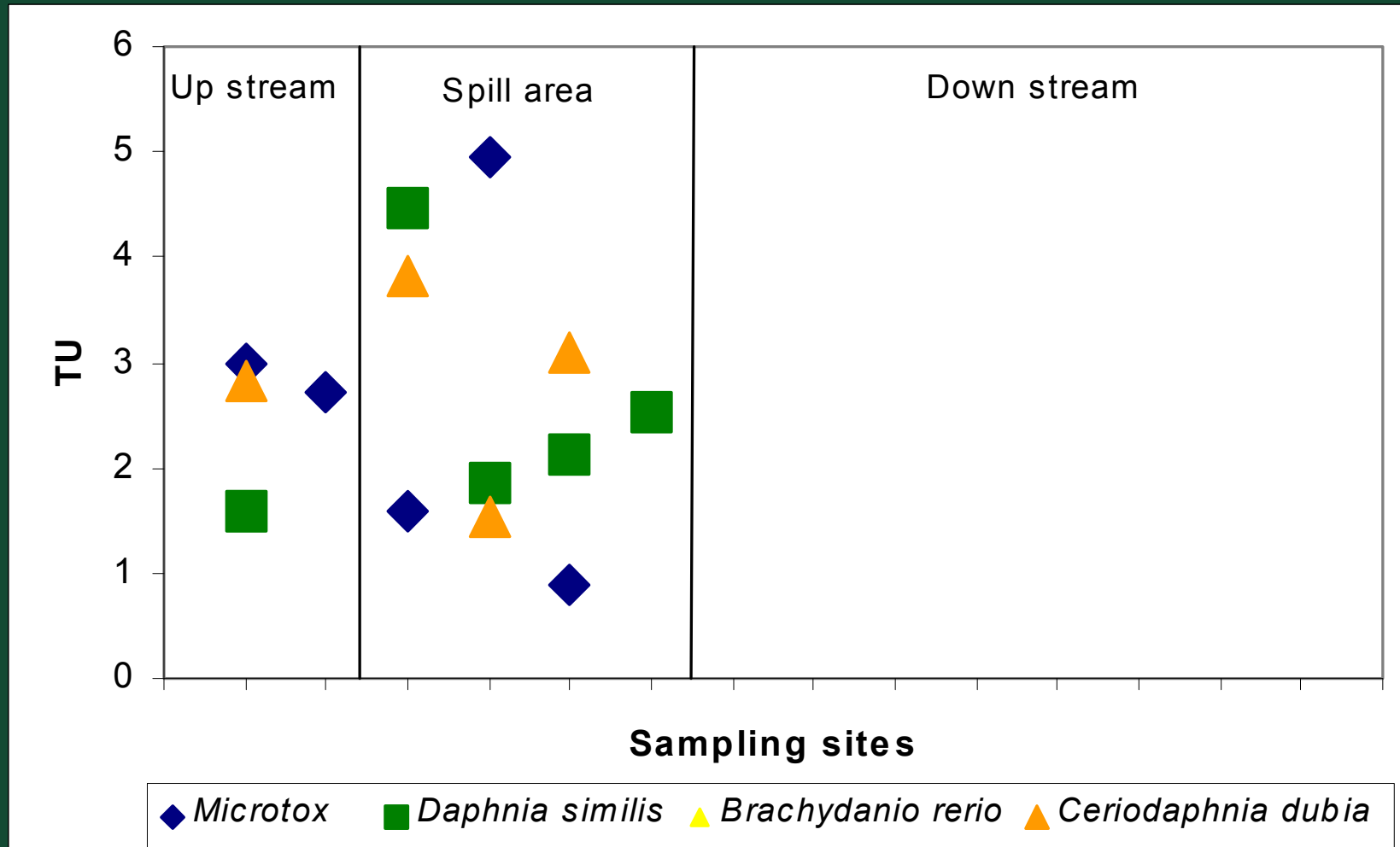
## PAH by GC-MS in rivers water

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 fisheri*  
*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

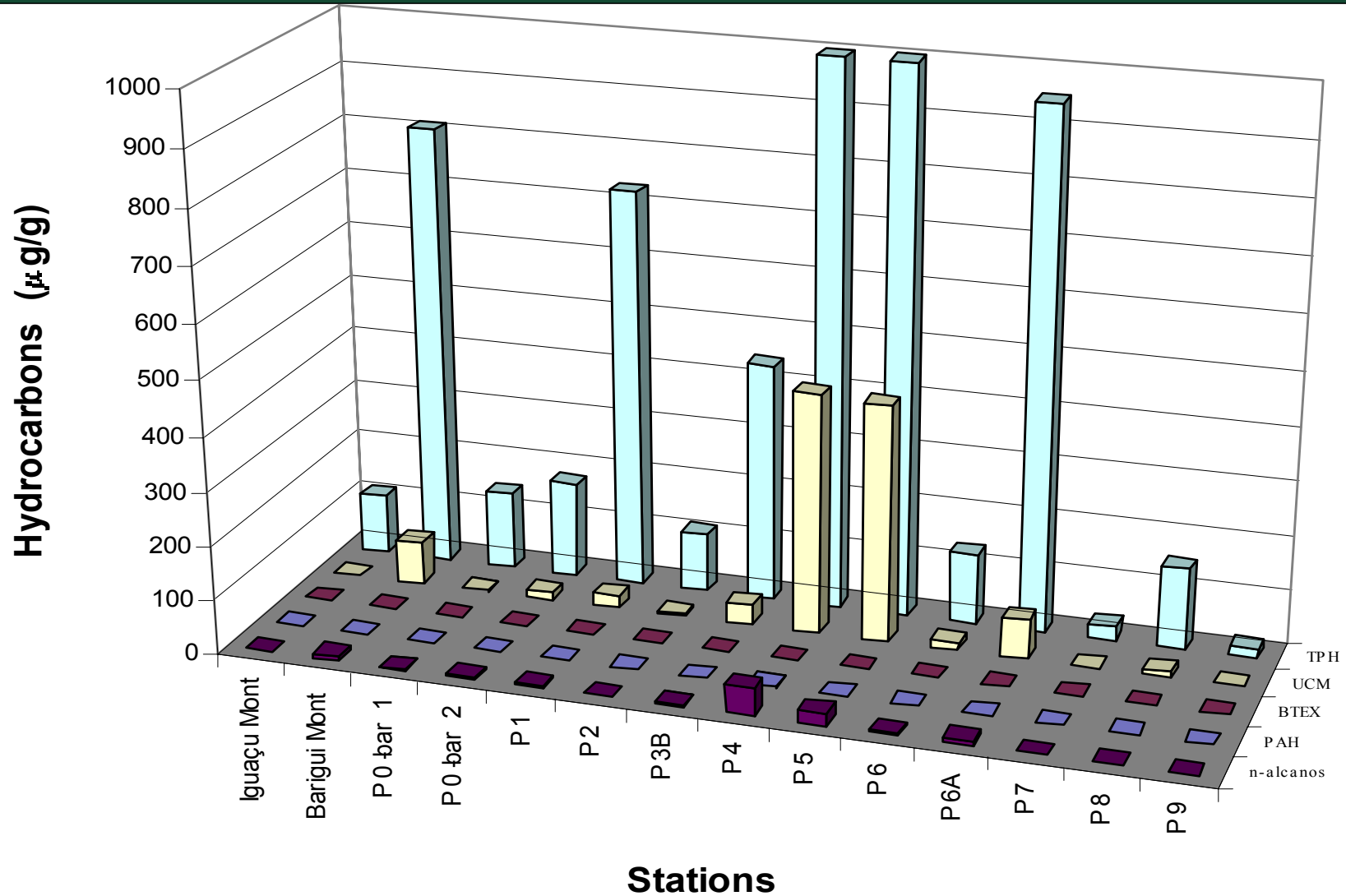
### Toxicological assays

(Microtox and *Daphnia similis*)



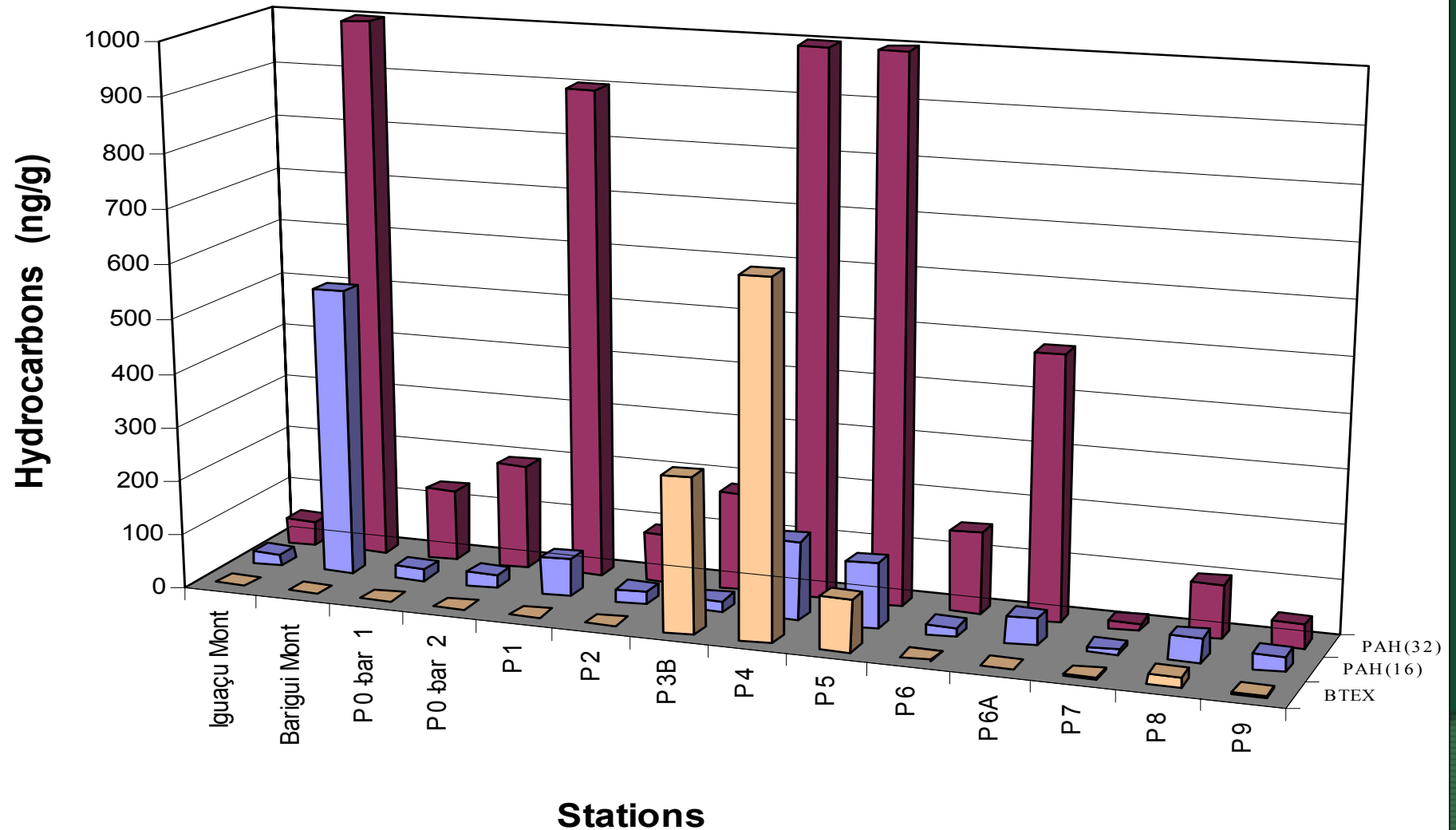


# Hydrocarbons in River Sediments - $\mu\text{g/g}$ (ppm)





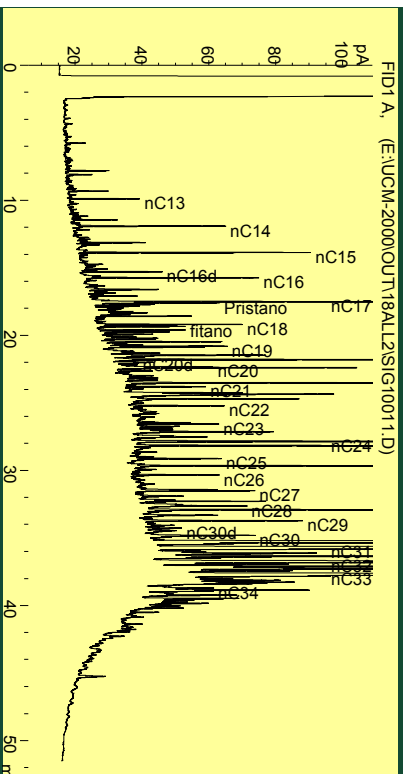
# Hydrocarbons in River Sediments - ng/g ( ppb)



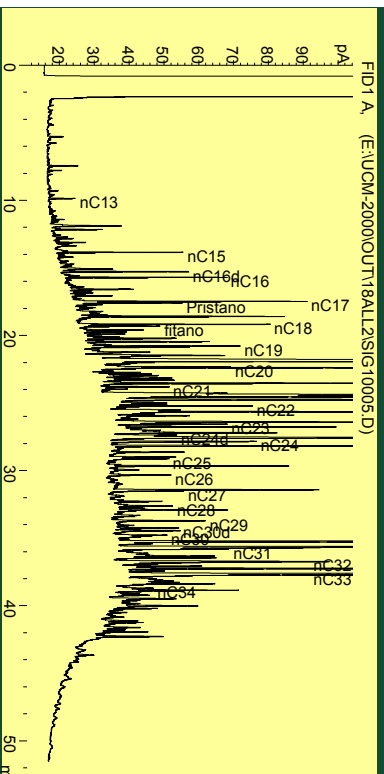
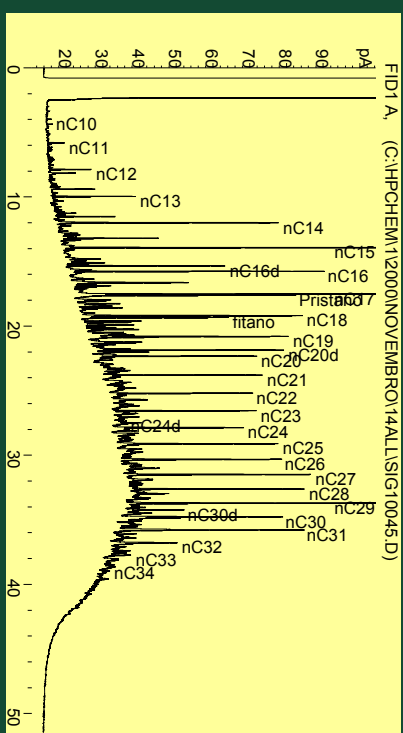


Iguassu River oil spill - July/2000

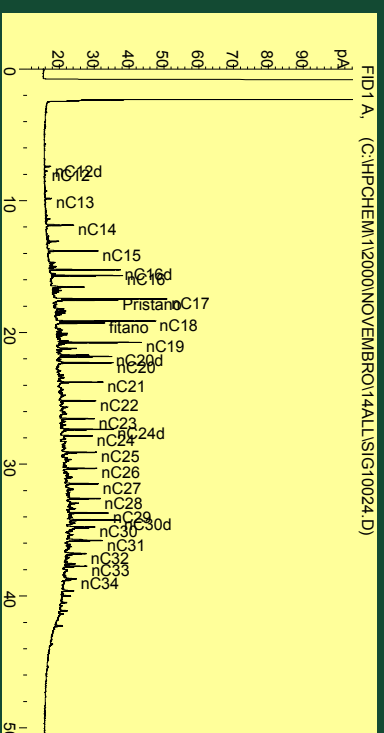
# Fingerprinting of Sediment extracts (GC-FID)



P4 - Guajuvira  
22/Aug/00



Total extract (TEM)



n-alkanes (after cleanup)

Barigui River  
upstream  
24/Aug/00

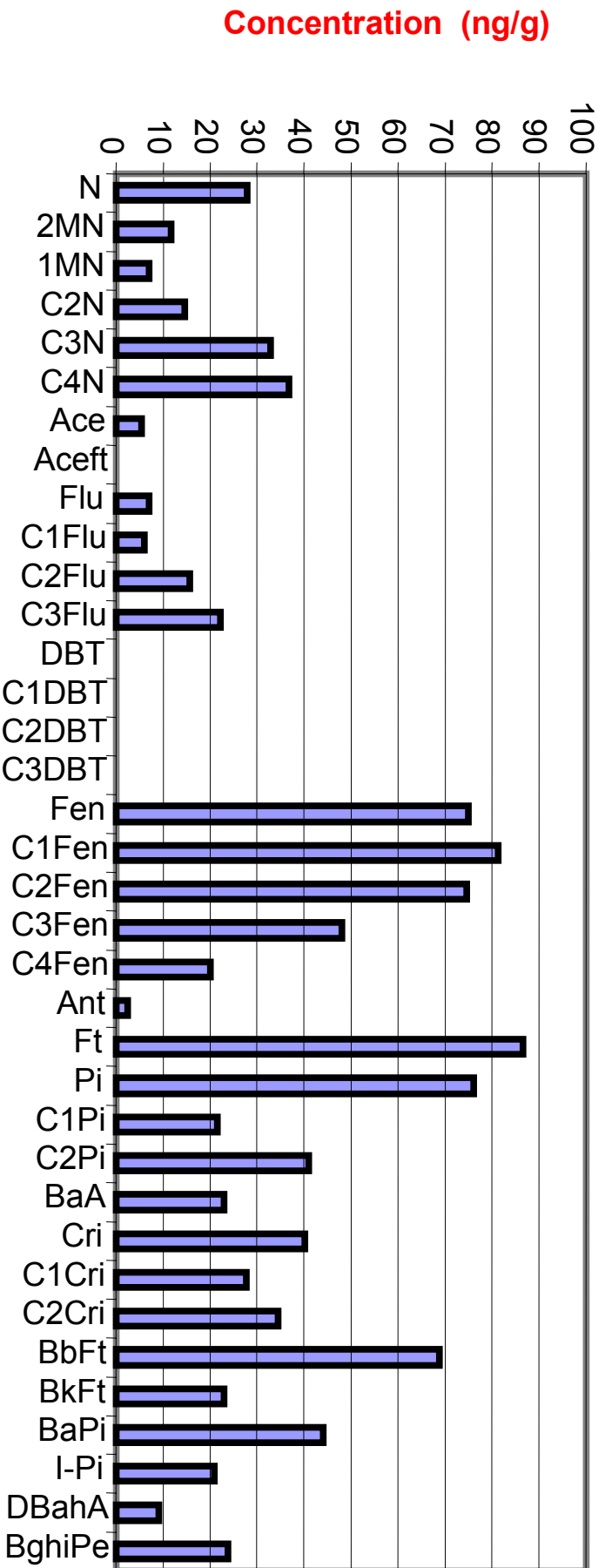




Iguassu River oil spill - July/2000

# PAH in sediment by GC-MS

## UPSTREAM BARIGUI RIVER

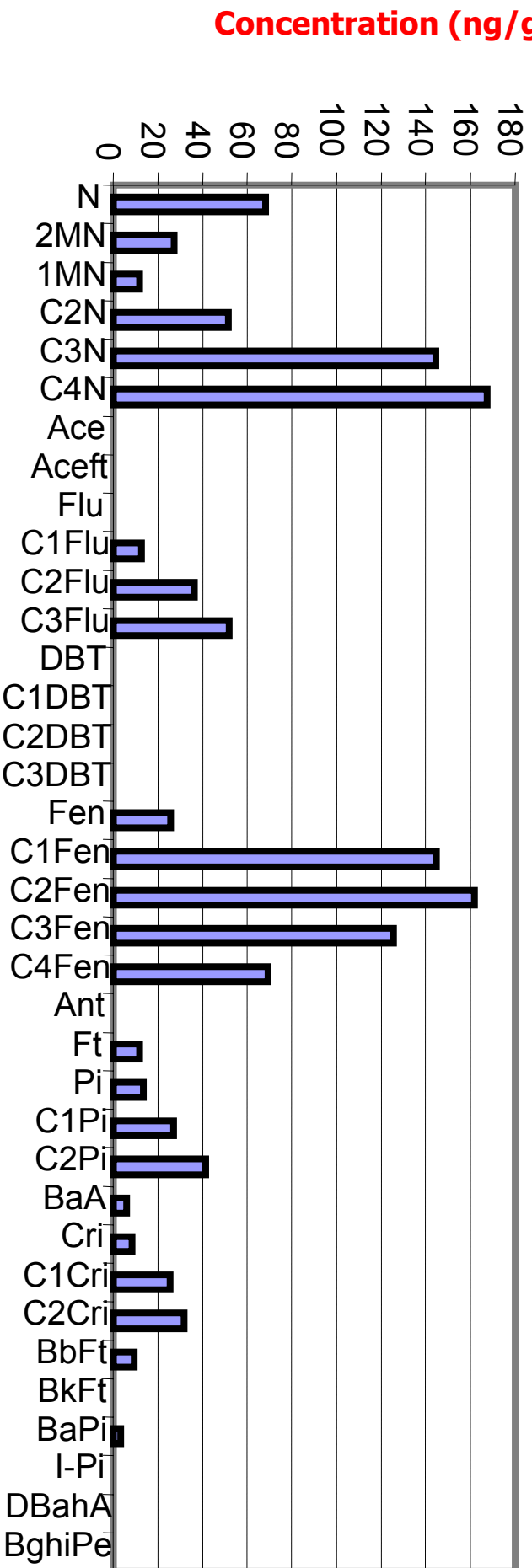




Iguassu River oil spill - July/2000

# PAH in sediment by GC-MS

Station P4- Guajuvira





## PAHs in Sediments - Literature Comparison

### Iguassu and Barigui Rivers:

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

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

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

GC-MS  
(sum 36 PAH)

### Other brazilian rivers:

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

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

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

HPLC - UV  
only the 16 PAH



## Toxicity of the sediments leaching

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

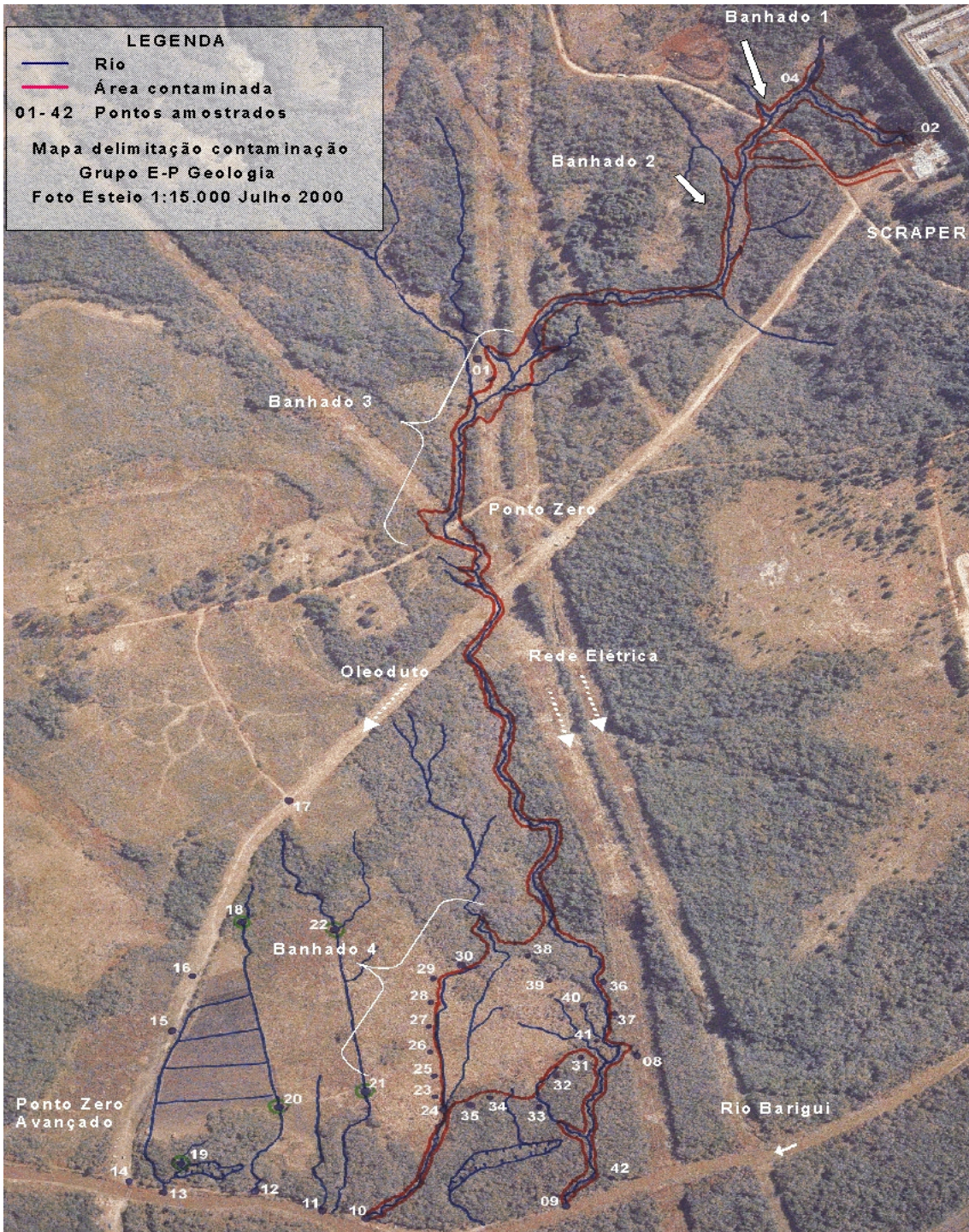




## GENERAL CONCLUSION

### 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 m<sup>2</sup>);**
- **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.**