

# The Geochemistry of Platinum in an Urban Estuary (NW Iberian Peninsula)

Antonio Cobelo-García

Grupo de Bioquímica Mariña. Instituto de Investigacións Marinas Vigo (IIM-CSIC), Spain



## Background

The use of platinum group elements (PGE: Pt, Pd, Rh) in the catalytic converter of motor vehicles involves 50-60% of the total World demand for Pt and Pd and nearly 100% for Rh

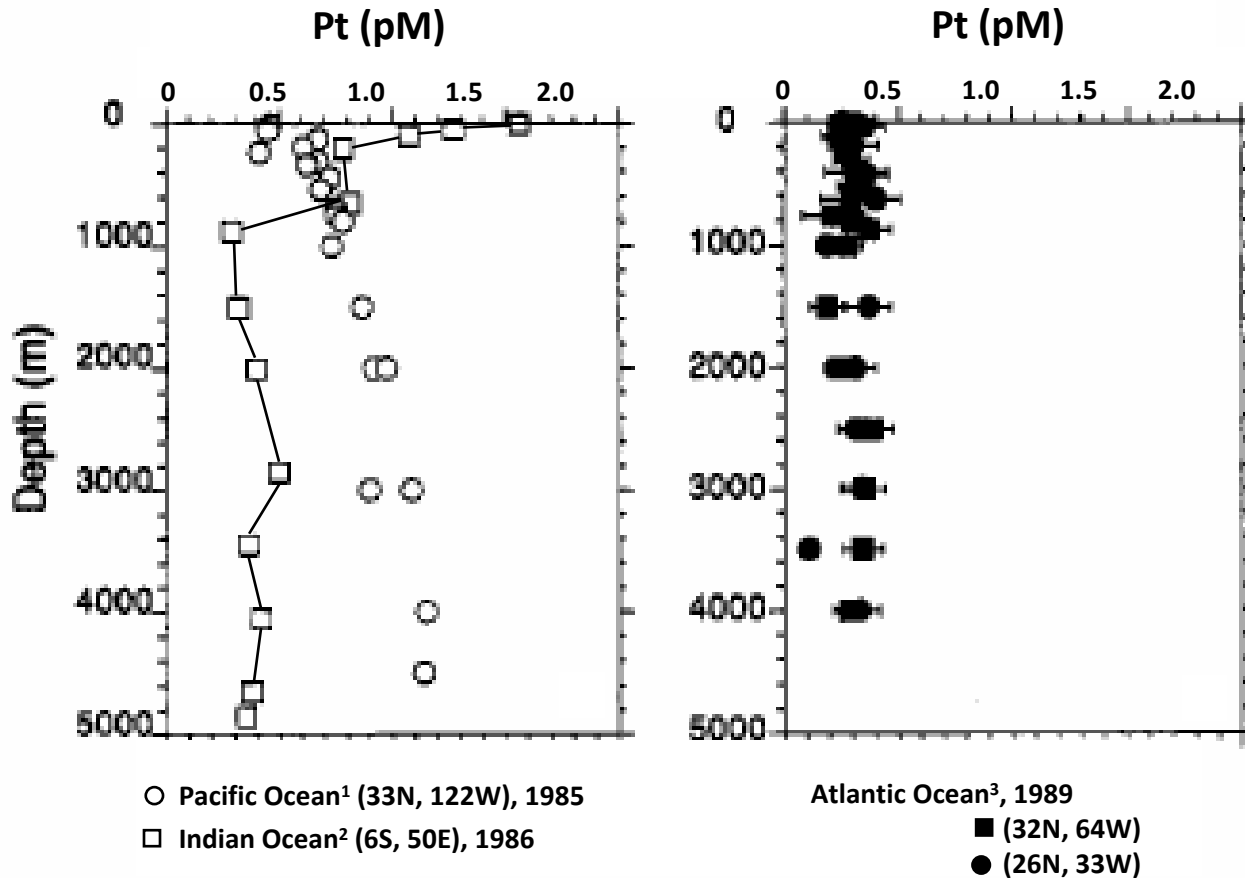
During abrasion and aging of the washcoat layer of the catalyst, metallic and oxide forms of PGE are emitted as particles

As a consequence, PGE concentrations above background values have been reported even in remote areas (e.g. Greenland) evidencing a long range transport

In this context, rivers, estuaries and coastal waters are, directly or indirectly, recipients of both point and diffuse inputs of PGE.

An understanding of the post-depositional mobility (interaction/complexation with naturally occurring ligands) and geochemical behaviour of PGE in the aquatic environment is, therefore, required

# Previous Studies on Pt in Seawater



<sup>1</sup>Goldberg, E.D., et al. *Appl. Geochem.* 1, 227 (1986)

<sup>2</sup>Jacinto, G.S., van den Berg, C.M.G. *Nature* 338, 332 (1989)

<sup>3</sup>Colodner, D.C., et al. *Anal. Chem.* 65, 1419 (1993)

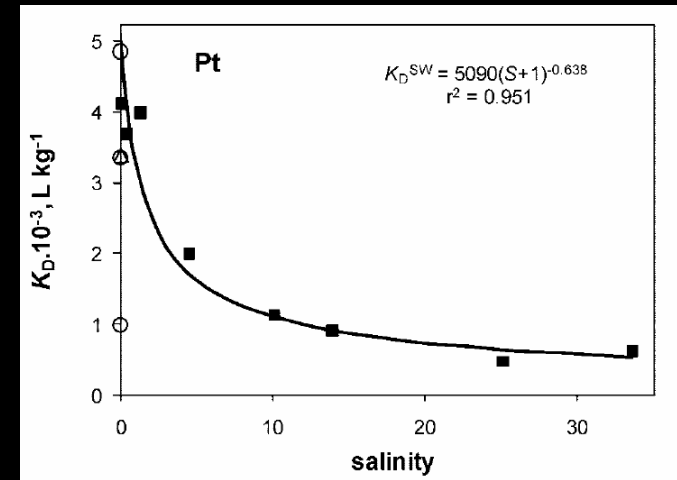
Different Oceanographic Behaviour

Few studies,  $\geq 20$  years

# Previous Studies on Pt in Estuarine Waters

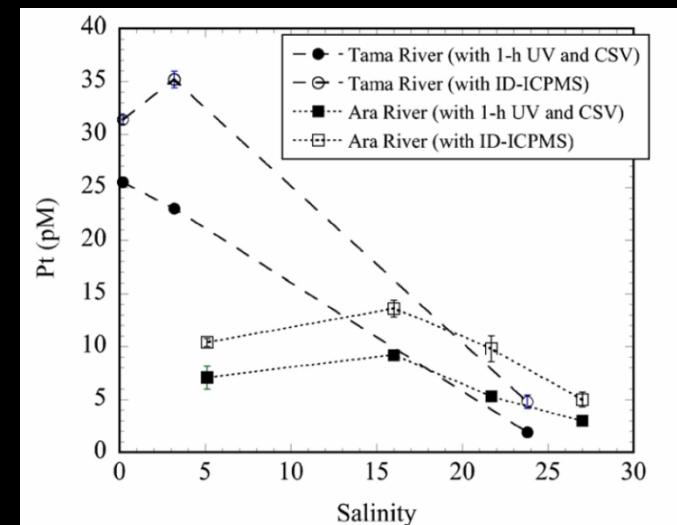
## A. Turner Group (University of Plymouth, UK)

Particle-Water Interactions under Estuarine Conditions  
 - Based on Spiking Experiments  
 (e.g. Cobelo-García et al., *Environ. Sci. Technol.* 42, 1096 (2008); Turner & Wu, *Mar. Chem.* 107, 295 (2007); Couceiro et al., *Mar. Chem.* 107, 308 (2007))



## H. Obata Group (University of Tokyo, Japan)

Reported Dissolved Pt Concentrations in the Tama and Ara Rivers (Bay of Tokyo)  
 (Obata et al., *Anal Chim. Acta* 580, 32 (2006))



## Aims of the Study

To provide a complete dataset of Pt concentrations in the dissolved ( $<0.2 \mu\text{m}$ ) and particulate ( $>0.2 \mu\text{m}$ ) in an urban estuary, and evaluate the impact of urban contamination

To characterize the speciation of Pt in the dissolved ( $<0.2 \mu\text{m}$ ), e.g. hydrophobic organic complexes (use of C18 columns)

To characterize the distribution and geochemical behaviour of Pt during estuarine mixing

To evaluate the post-depositional mobility of Pt arising from urban dust

# Area of Study

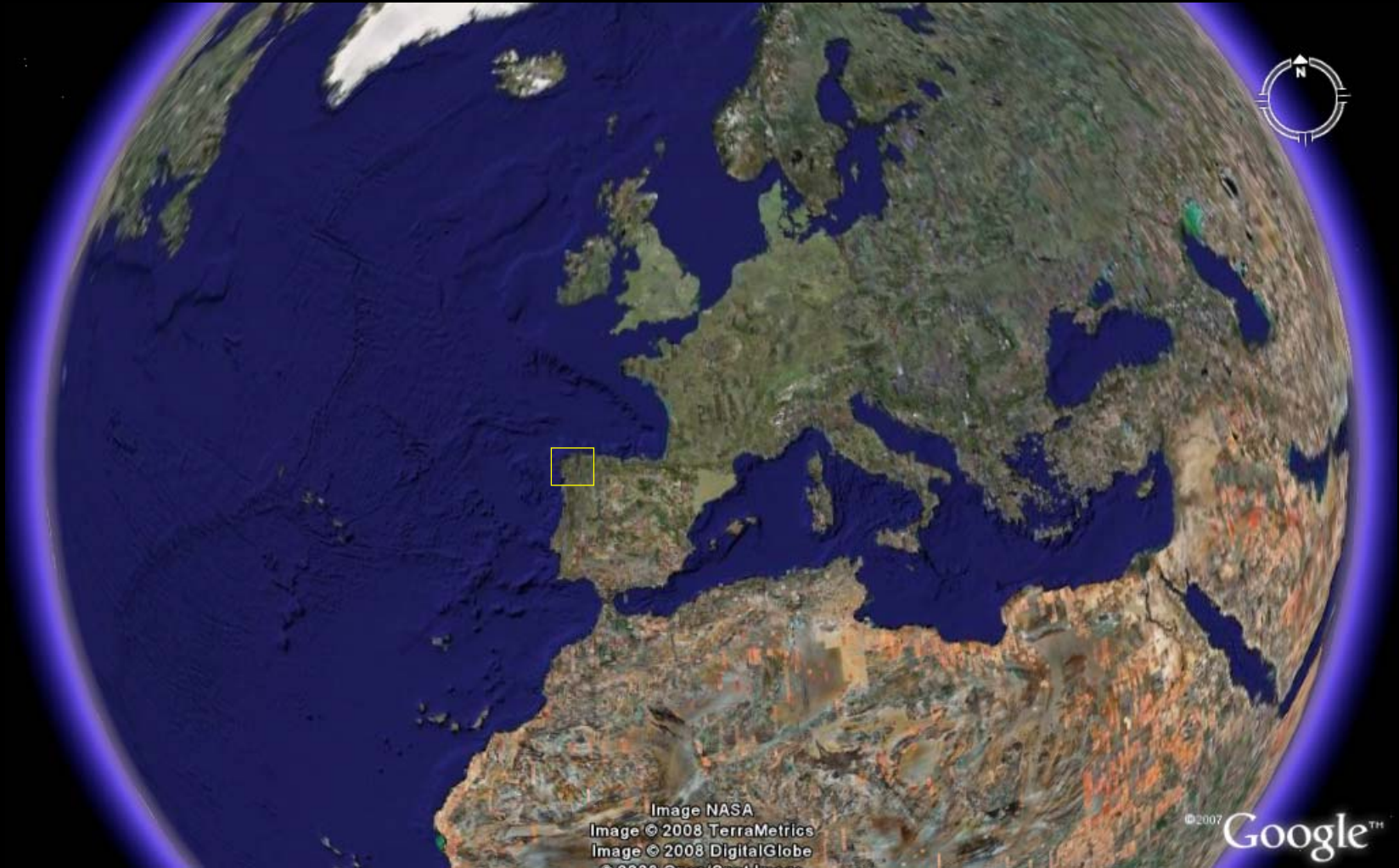


Image NASA  
Image © 2008 TerraMetrics  
Image © 2008 DigitalGlobe

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## Area of Study – The Pontevedra Ria



# Area of Study – Sampling Points

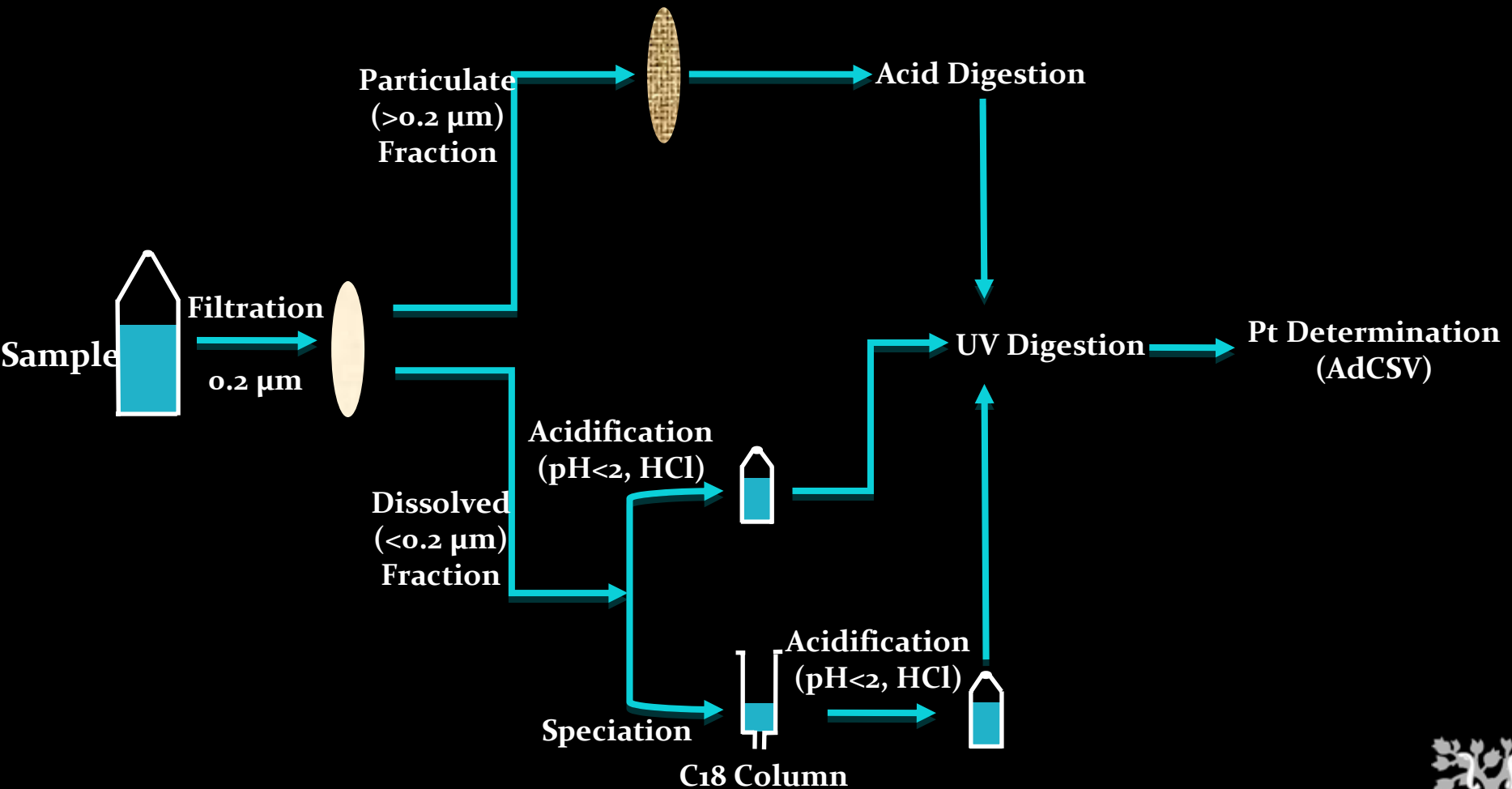




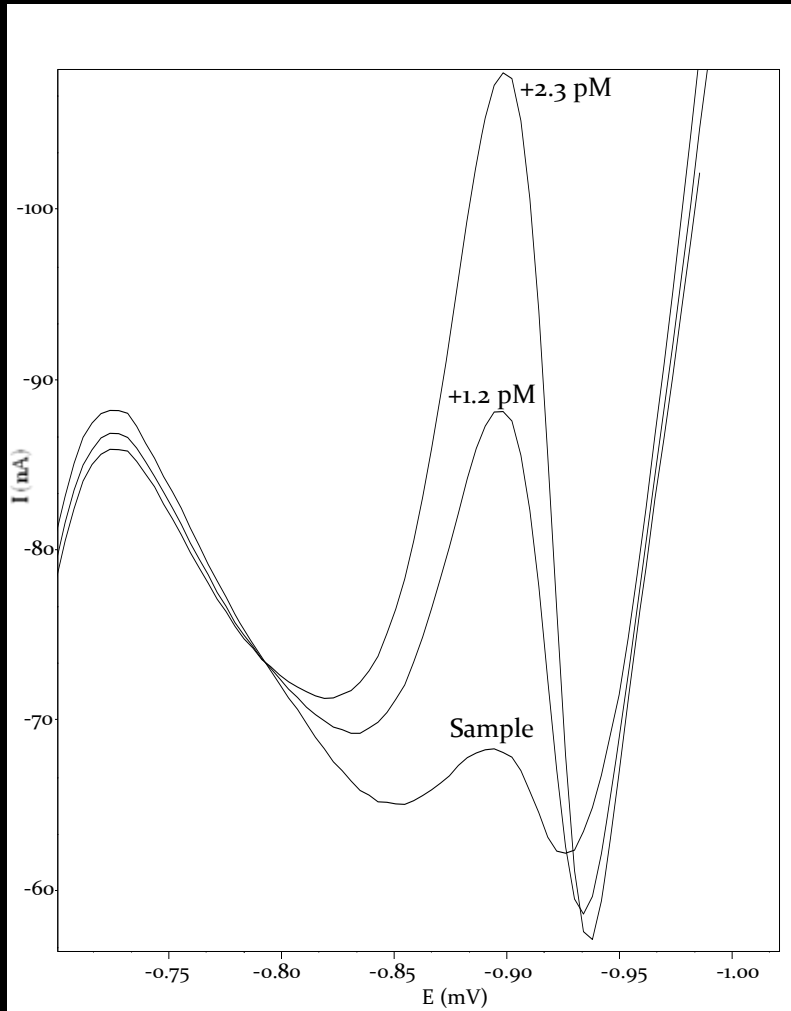
# Area of Study – Sampling Points



# Experimental Procedure



# Determination of Pt using Catalytic Adsorptive Cathodic Stripping Voltammetry



Determination of Pt in an Estuarine Sample.  
Deposition Time: 200 s. Sample Concentration: 0.27 pM

Conditions:

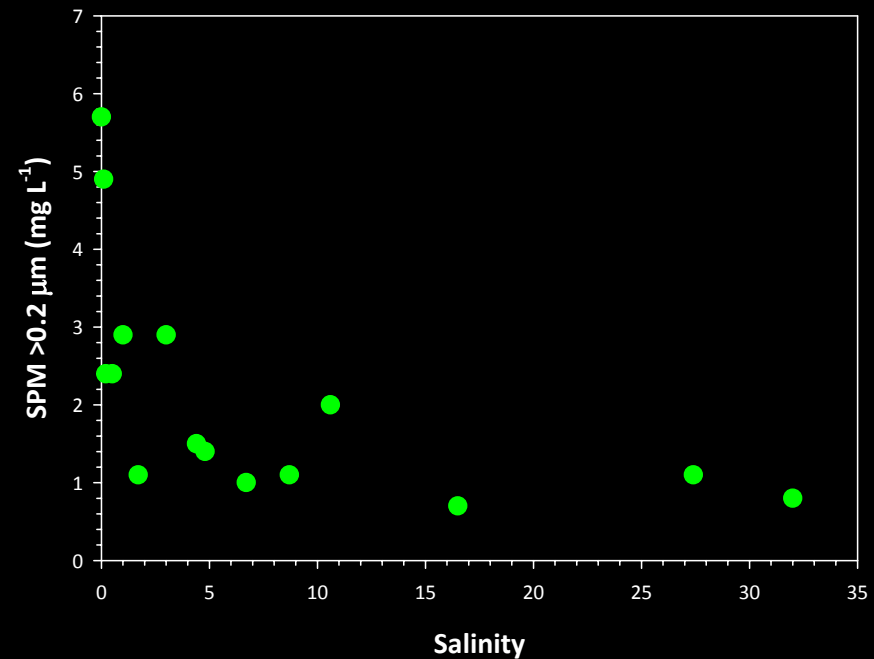
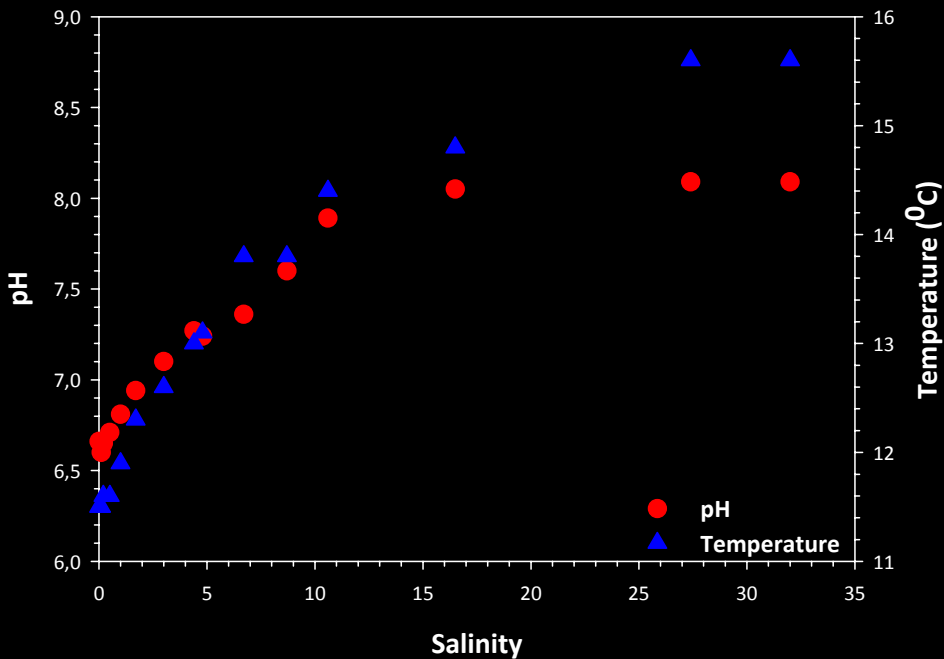
0.6 M H<sub>2</sub>SO<sub>4</sub>  
0.45 mM Hydrazine  
3.5 mM

Formaldehyde

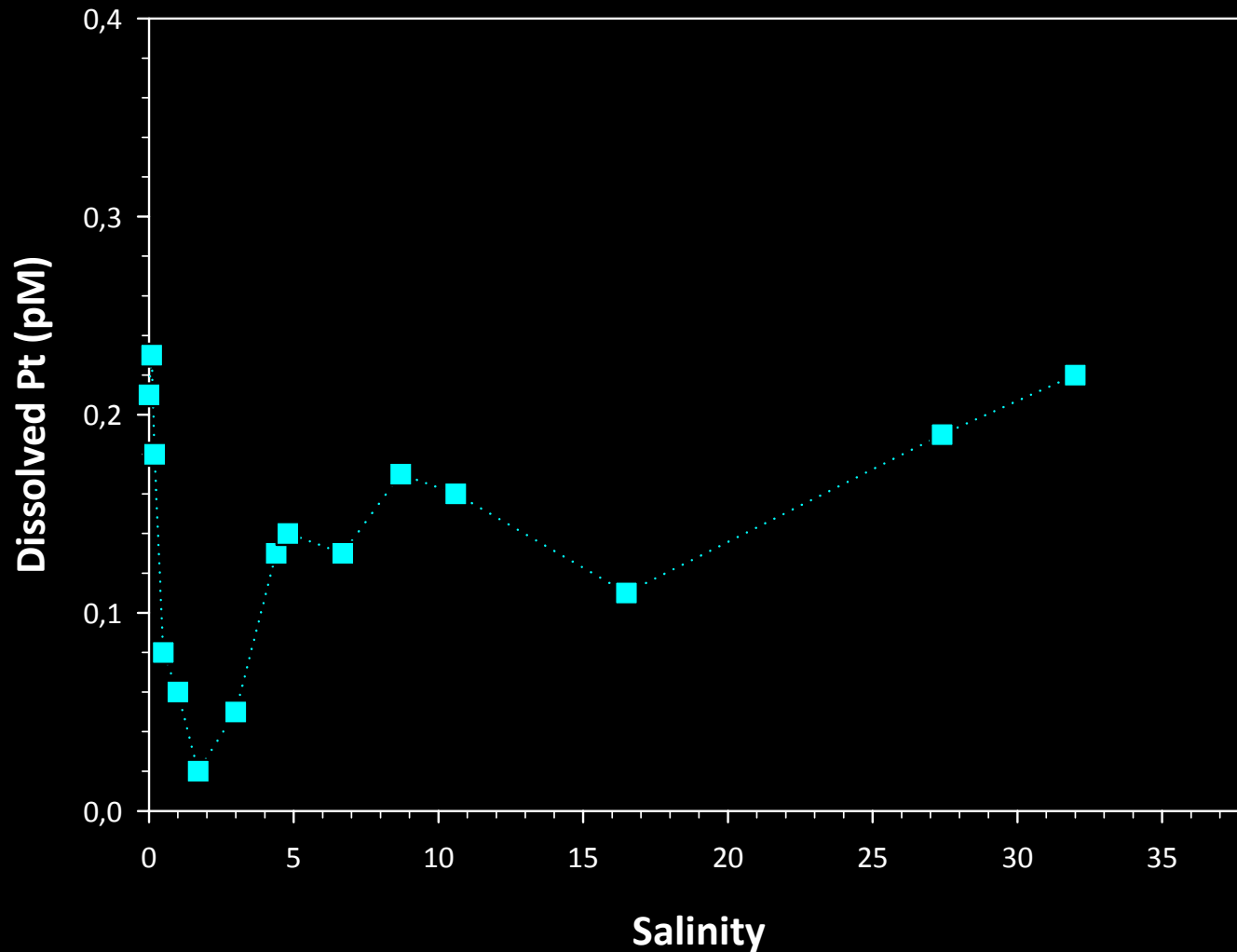
Deposition Potential: -0.30 V  
Deposition Time: 200-600 s

Procedural Blank:  $65 \pm 15$  fM (n = 6)  
Detection Limit (3·SD): 0.045 pM

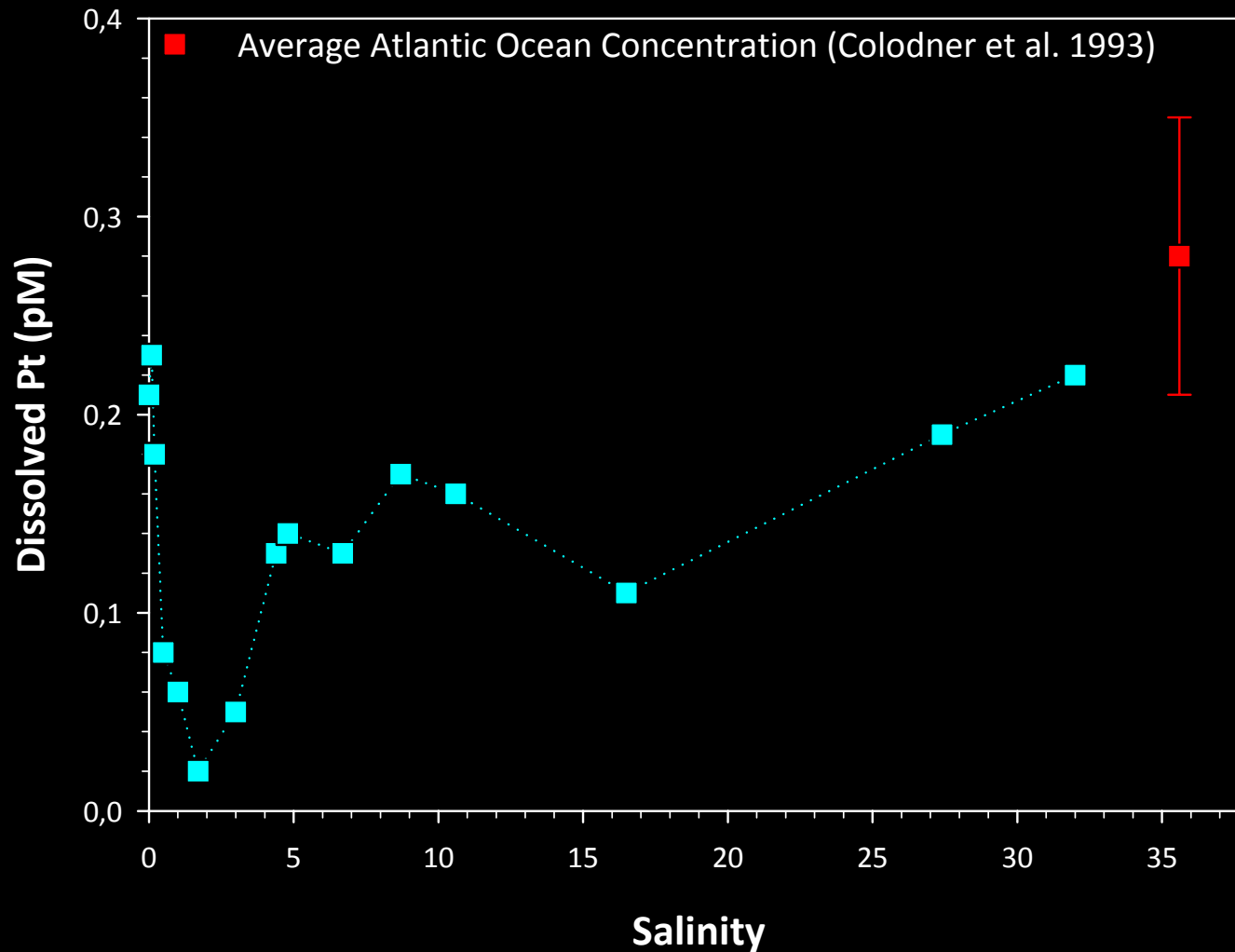
## Results: Ancillary Parameters



## Results: Dissolved (&lt;math&gt;&lt;0.2 \mu\text{m}&lt;/math&gt;) Pt Distribution during Estuarine Mixing



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## Conclusions

**Dissolved Pt shows a well-defined estuarine distribution, with removal at the low-salinity zone and mid-estuarine addition**

**The increase in dissolved Pt concentrations at high salinities leads to values consistent with the previously reported for the Atlantic Ocean**

**The values obtained indicate a null impact of urban contamination on dissolved Pt  
Concentrations are 1-2 orders of magnitude lower than those previously reported for other World urban rivers and estuaries**

**Pending analysis of the particulate fraction and the hydrophobic dissolved Pt will shed more light on its geochemical estuarine behaviour**

**Thanks for your attention**