



**NATURAL RESOURCES CANADA - INVENTIVE BY NATURE**

# **Method Development for Determining the Removal of Metals from the Water Column under Transformation/Dissolution Conditions for Chronic Hazard Classification**

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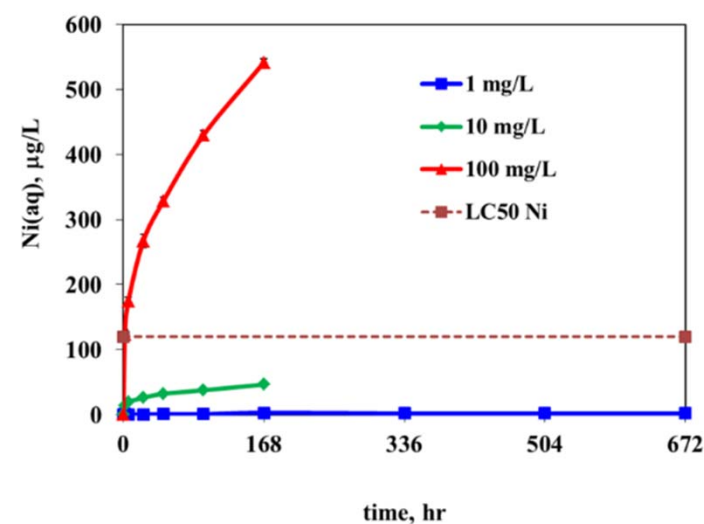
# Objective of project:

- To determine if an extension of the T/DP method (T/DP-E) could be used for assessing environmental transformations of metals in the water column, mentioned in the UN GHS and EU CLP classification systems. The T/DP method was extended with 2 parts:
  - T/DP-E Part 1, to measure binding of metals to a substrate and subsequent settling
  - T/DP-E Part 2, to assess the remobilization of metals following resuspension of substrate



# Transformation/Dissolution Protocol:

- Method to determine the rate and extent at which a metal, sparingly soluble metal compound or alloy will release metal-bearing ions to an aqueous environmental medium;
- Aqueous T/D media based on OECD 203 medium for toxicity testing of fish and *Daphnia*;
- Compare T/D metal concentrations with Ecotoxicity Reference Values to derive aquatic hazard classification levels within the framework of the UN GHS;
- Method has been successfully applied to derive aquatic hazard classifications on concentrates, mattes, alloys, metal powders and massives and metal compounds.



# Extended T/DP (T/DP-E) Part 1

- Following the main elements of the T/DP sampling routine:
  - 1 L Schott Duran flasks with 1 mg/L dissolved metal in 10x dilute OECD 203 aquatic medium - pH 6
  - Procedural blanks and triplicates;
  - Bubbled with 0.5% CO<sub>2</sub> balanced with air;
  - 10 g of low binding substrate (LBS) added to flasks (except blanks), 1 min agitation;
  - Sampling intervals at 0, 2, 6, 24, 48, 96, 168, 336, 504 and 672 hrs;
  - Analysis of dissolved and total metals, Fe;
  - Measured pH, D.O. and temperature;
  - Replenish flasks after sampling;
  - Aqueous samples filtered through a 0.2 micron filter.

Continuous  
aeration with  
0.5% CO<sub>2</sub>-  
balance air



1 L 10x dilute  
OECD pH 6  
freshwater

10 g of sediment

# Substrate composition

- Average, 10<sup>th</sup> and 90<sup>th</sup> percentiles of sediment parameters of relevance to metal transport derived from European data (ARCHE 2013)

Percentile	Fe (Aqua R) %	TOC %
P10	0.75	1.3 (0.3 - 2.3)
Average	2.25	3.7 (1.8 - 5.9)
P90	4	6.7 (3.8 - 11)



## Analysis

ID	Grain size	Type	Fe (Aqua R) wt%	TOC (%)	TC(%)
LBS	medium sand	Stream	1.56	1.2	1.1
IBS	coarse sand	Stream	3.61	2.5	3.4
HBS	silt/clay	Lake	5.98	3.3	3.1

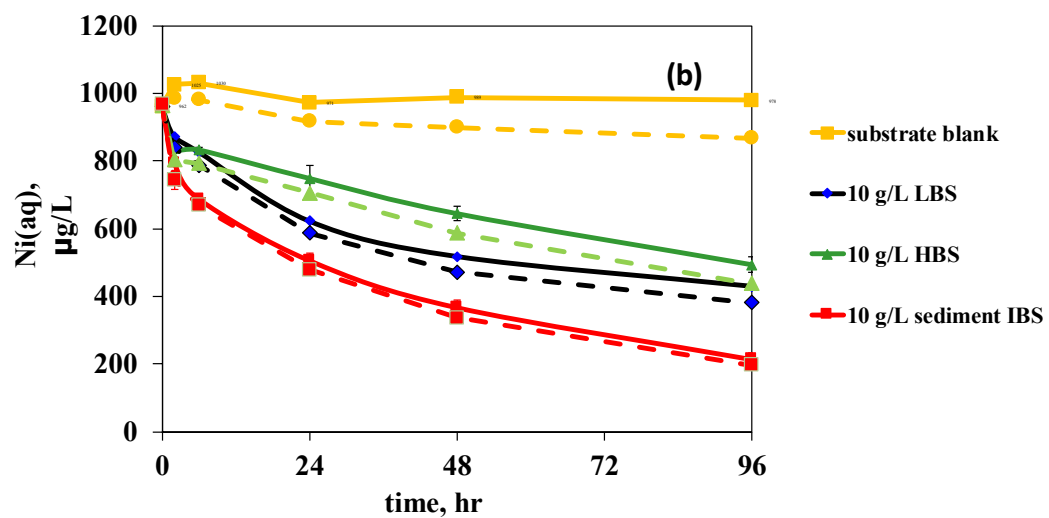
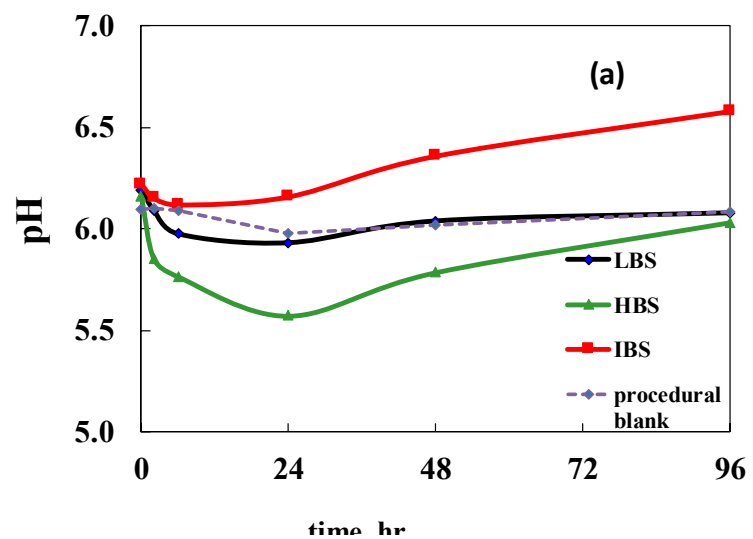
ID	Co (ppm)	Mn (ppm)	Ni (ppm)	Ag(ppm)	Cu (ppm)	Zn (ppm)	Pb (ppm)
LBS	11.9	506	34	0.05	18	54.7	13.5
IBS	17.4	1413	62	0.26	17		21.4
HBS	36.3	1147	94.6	0.23	87	14.5	15.0



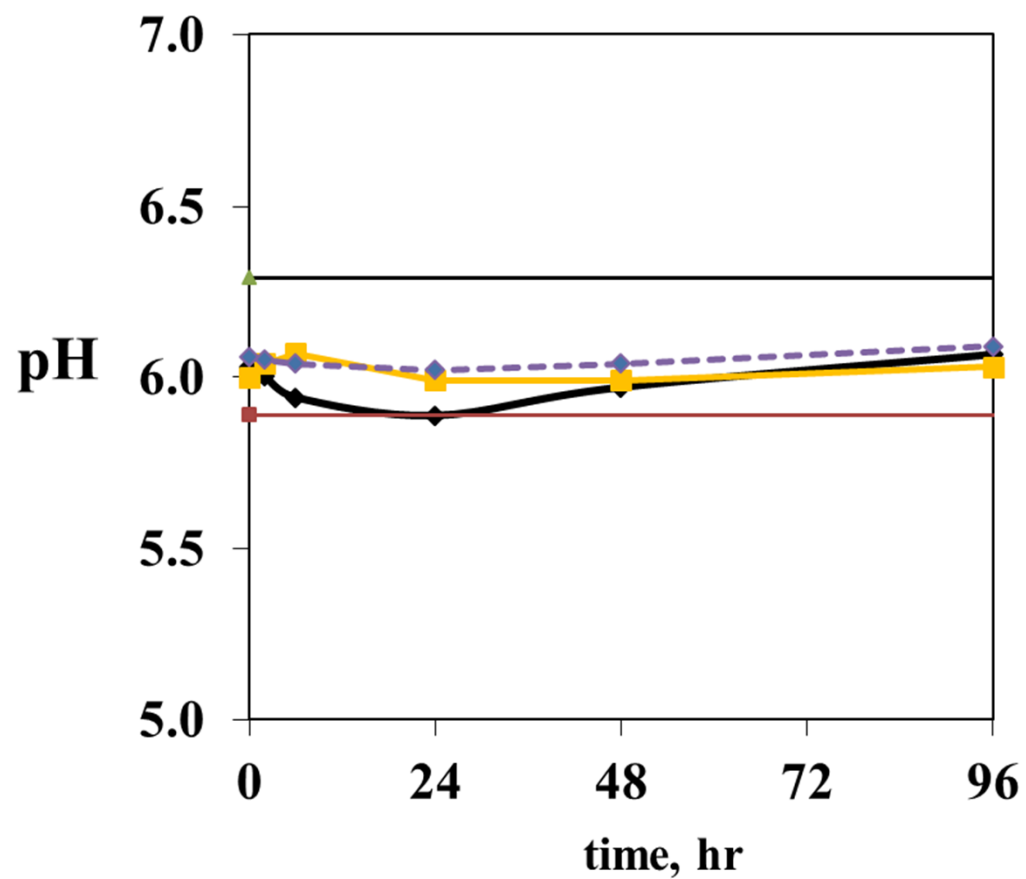
# Substrate loading

- Add 10 g of substrate, agitate for 1 min
- Assuming:
  - TSS = total suspended solids concentration in the water column is 15 mg/L
  - $v_s$  = solids settling velocity = 2.5 m/d which is the default settling velocity in the EUSES model
  - $F_s$  = settling flux =  $(15 \text{ g/m}^3) * (2.5 \text{ m/d}) = 37.5 \text{ g/(dm}^2)$
  - $M$  = total solids transported to sediment =  $(37.5 \text{ g/(dm}^2)) * (28 \text{ d}) = 1,050 \text{ g/m}^2$
  - $TSS_{\text{flask}} = M * A_{\text{flask}} / V_{\text{flask}} = (1,050 \text{ g/m}^2) * (0.0071 \text{ m}^2) / (1 \text{ L}) = 7.5 \text{ g/L}$





# pH control

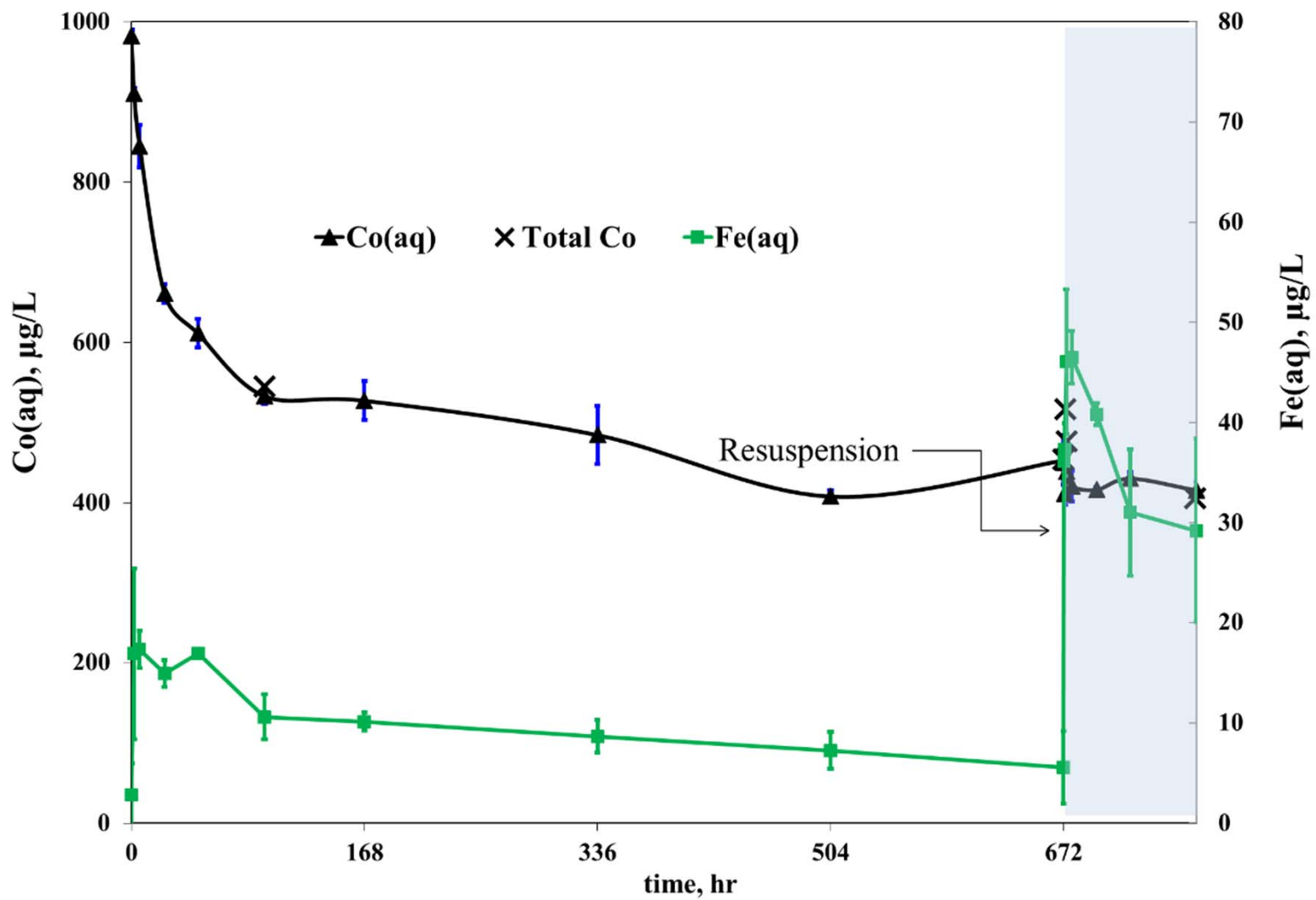


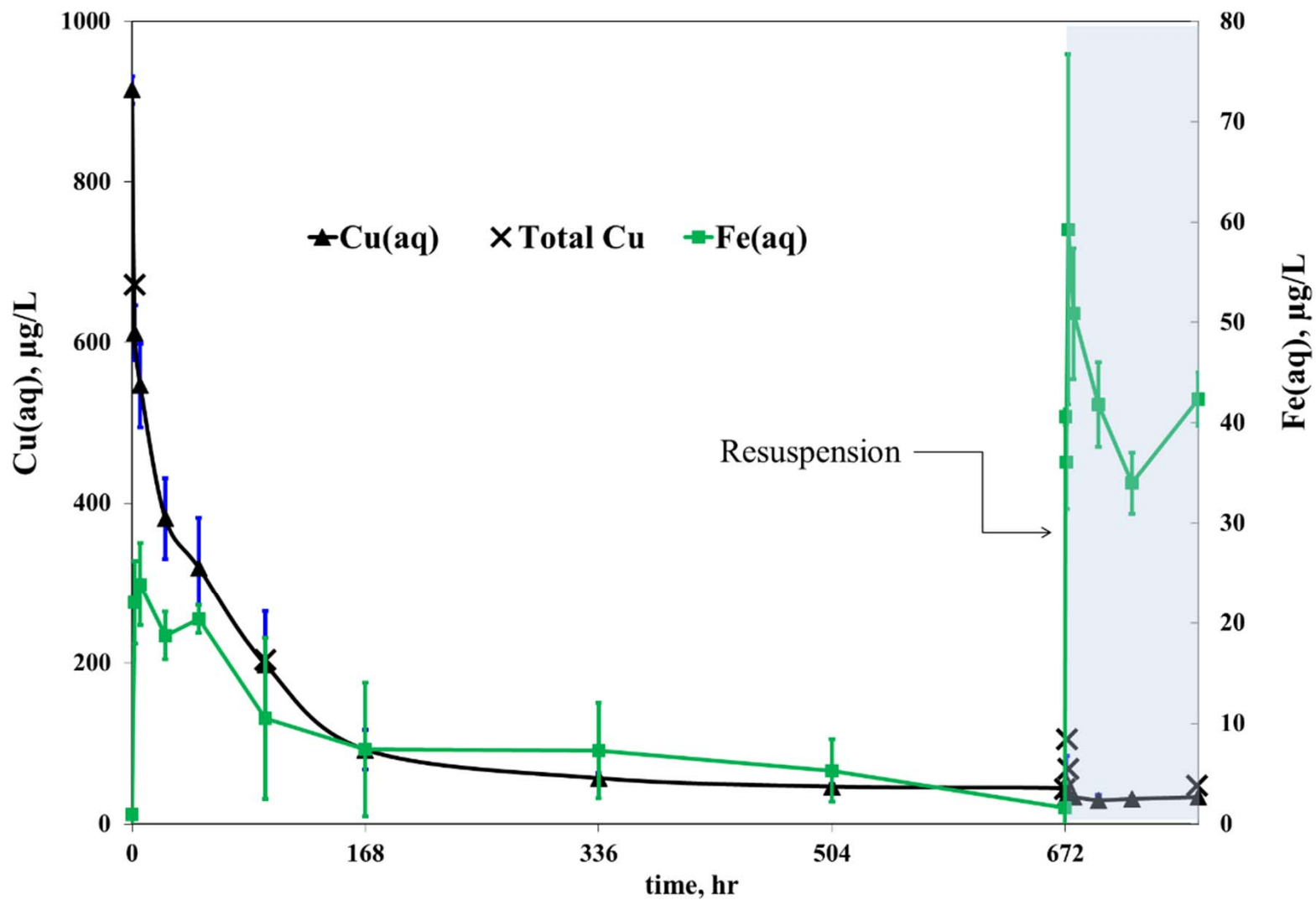


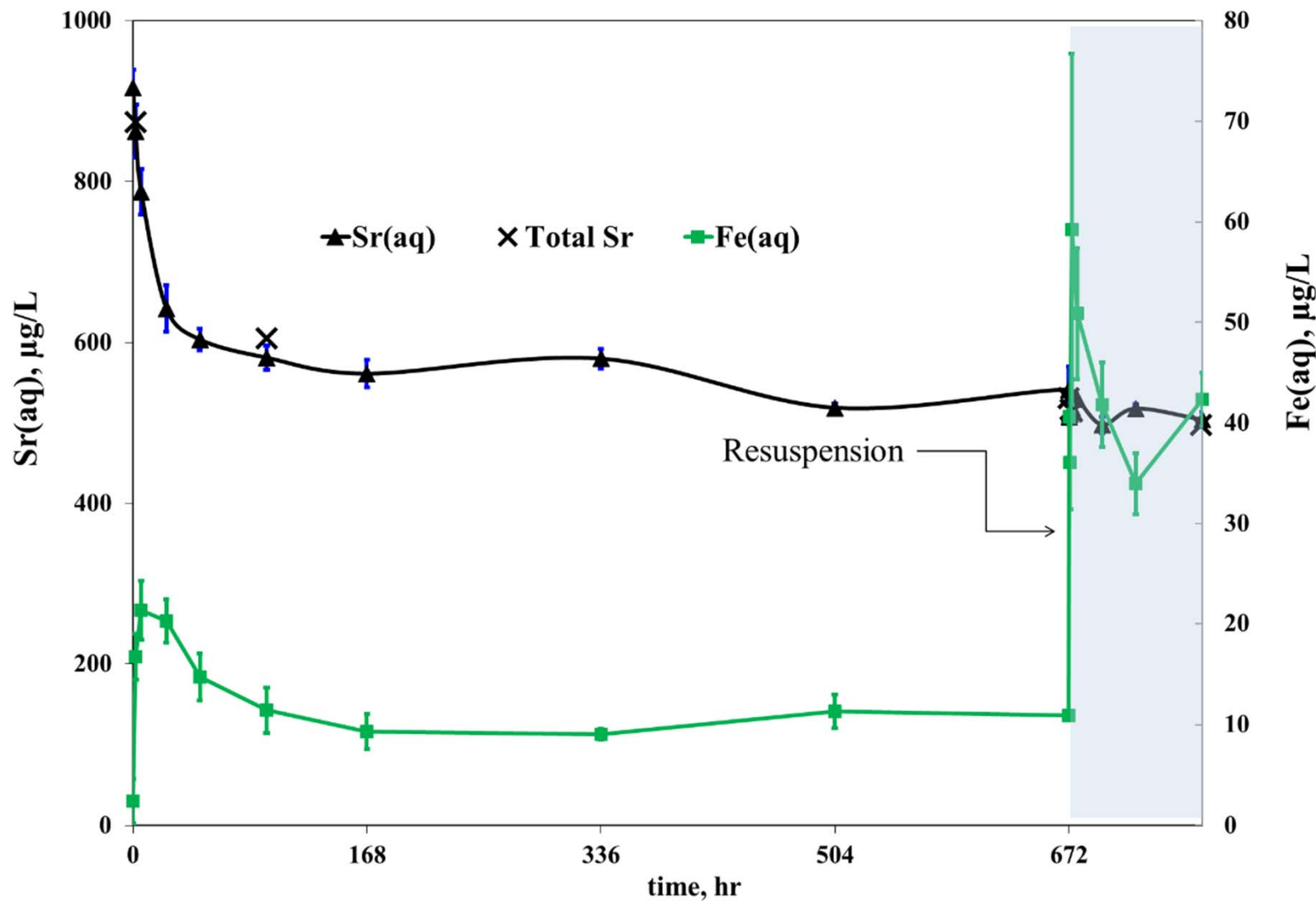
## Extended T/DP (T/DP-E) Part 2

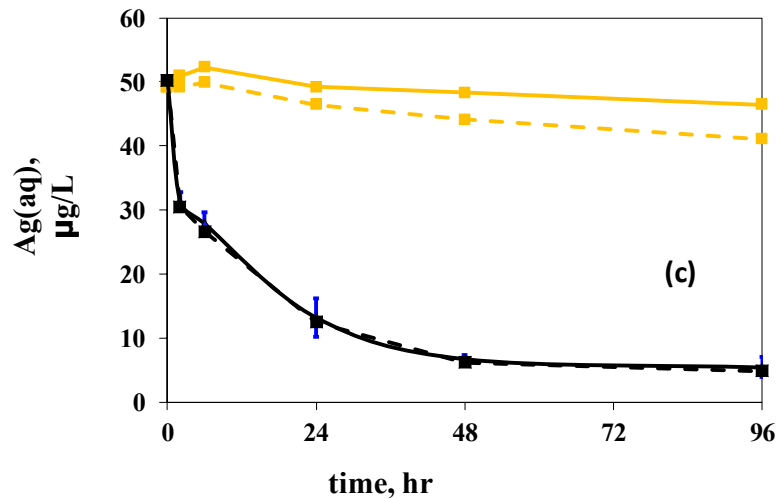
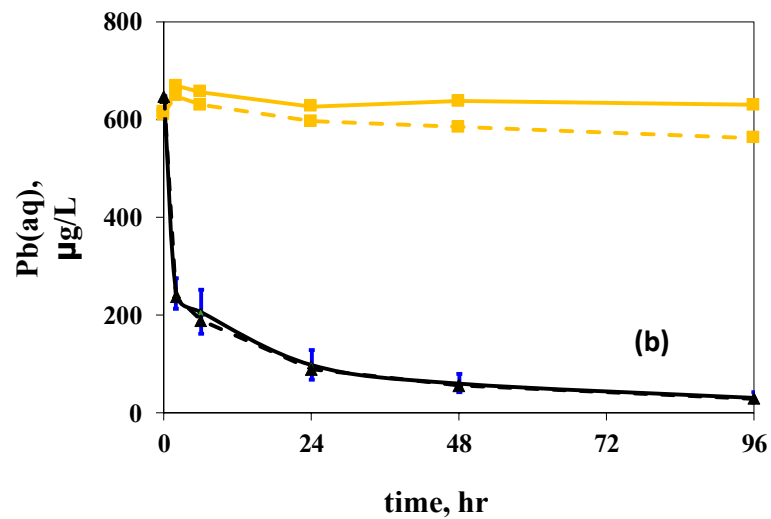
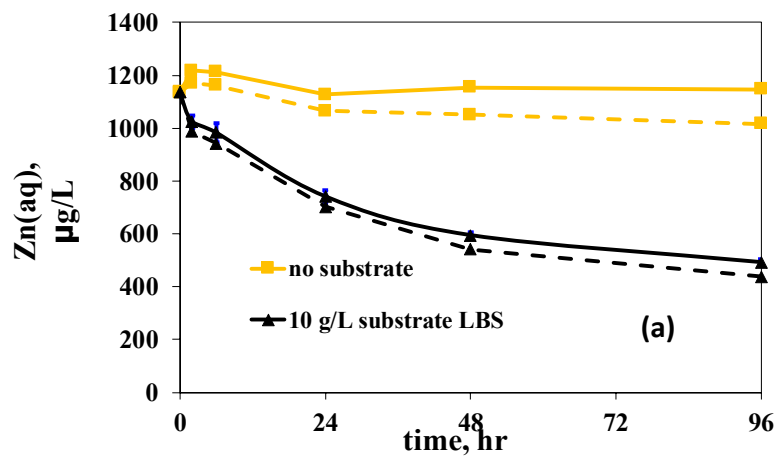
- After completion of the T/DP-E, part 1, the flasks are agitated at 150 rpm for 1 hour, to mimic a resuspension event;
- The solutions are sampled periodically at 0.5, 1, 2, 6, 24, 48, and 96h;
- Samples are analyzed for dissolved metal concentrations; selected samples are analyzed for total metal concentrations (including measurement of Fe as a fingerprint of the substrate);
- pH, dissolved oxygen concentration, and temperature.











# Conclusions

- Successful method development for measuring metal removal from the water column
- Key processes are reflected: metal binding to suspended solids, settling of metal associated to solids, initial diagenesis reactions
- Different metals exhibit different removal rates
- The T/DP Extension offers an experimental approach that may be useful to assess metal removal in the context of environmental hazard classification.



# Questions?

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