

Measuring the $\delta^{13}\text{C}$ Signature of Dissolved Organic Carbon: An Inter-laboratory Comparison Study

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Objectives

Much progress has been made towards precisely and accurately measuring the concentration of dissolved organic carbon (DOC) in the past 4 decades.

A number of oxidation methods have been developed, including:

1. High-temperature catalytic oxidation (HTC-DOC-IRMS)
2. Wet chemical oxidation (WCO-IRMS)
3. Liquid chromatography (LC-IRMS)
4. Solid phase extraction (SPE) followed by EA-IRMS

We called upon a number of laboratories to participate in an inter-comparison study to evaluate the applicability of these methods in measuring:

1. [DOC]
2. $\delta^{13}\text{C}$ of DOC

For:

1. Standards (known $\delta^{13}\text{C}$) and samples (unknown $\delta^{13}\text{C}$)
2. Freshwater and saltwater solutions

List of participants

Oxidation Method Used	Laboratory/Institution	Analysts
High Temperature Catalytic Oxidation	Concordia University	Andrew Barber / Karine Lalonde
	G. G. Hatch Lab (University of Ottawa)	Paul Middlestead
	UC Davis Stable Isotope Facility	Joy Matthews
	USGS / WHOI	John Pohlman
Wet Chemical Oxidation	Southern Cross University	Matheus Carvalho
	KU Leuven	Steven Bouillon
	FAU Erlangen-Nuremberg	Robert Van Geldern
	Vrije Universiteit Brussel	Natacha Brion
	NC State University	Chris Osburn
	UC Davis Stable Isotope Facility	Joy Matthews
WCO coupled to Gas Bench	ETH Zürich	Susan Lang
LC-IRMS	Université d'Orléans	Patrick Albéric
	NIOZ	Marco Houtekamer
	MARUM	Xavier Prieto / Marcus Elvert
Cavity Ring-Down Spectrometer	University of Malaga	Iñaki Vadillo
Solid Phase Extraction + EA-IRMS	ICBM Oldenburg	Thorsten Dittmar / Jutta Niggemann

We would like to express our sincerest gratitude to all participants and ISOGEOCHEM frequenters who used their precious instrument time to analyze the samples or personal time for discussing this project.

DOC Oxidation Methods

High temperature catalytic oxidation	Wet oxidation	LC-DOC
<ul style="list-style-type: none"> • Up to 1.8 mL injections • 680-720°C conversion of DOC in the solid-state/gas phase • Salt/matrix does not affect combustion 	<ul style="list-style-type: none"> • Tens of mLs of sample • Persulfate chemically oxidizes DOC (100°C) • Competition between DOC and Cl⁻ for the persulfate reagent 	<ul style="list-style-type: none"> • 100 - 200 μL injections • Persulfate chemically oxidizes DOC (100°C) • Competition between DOC and Cl⁻ for the persulfate reagent

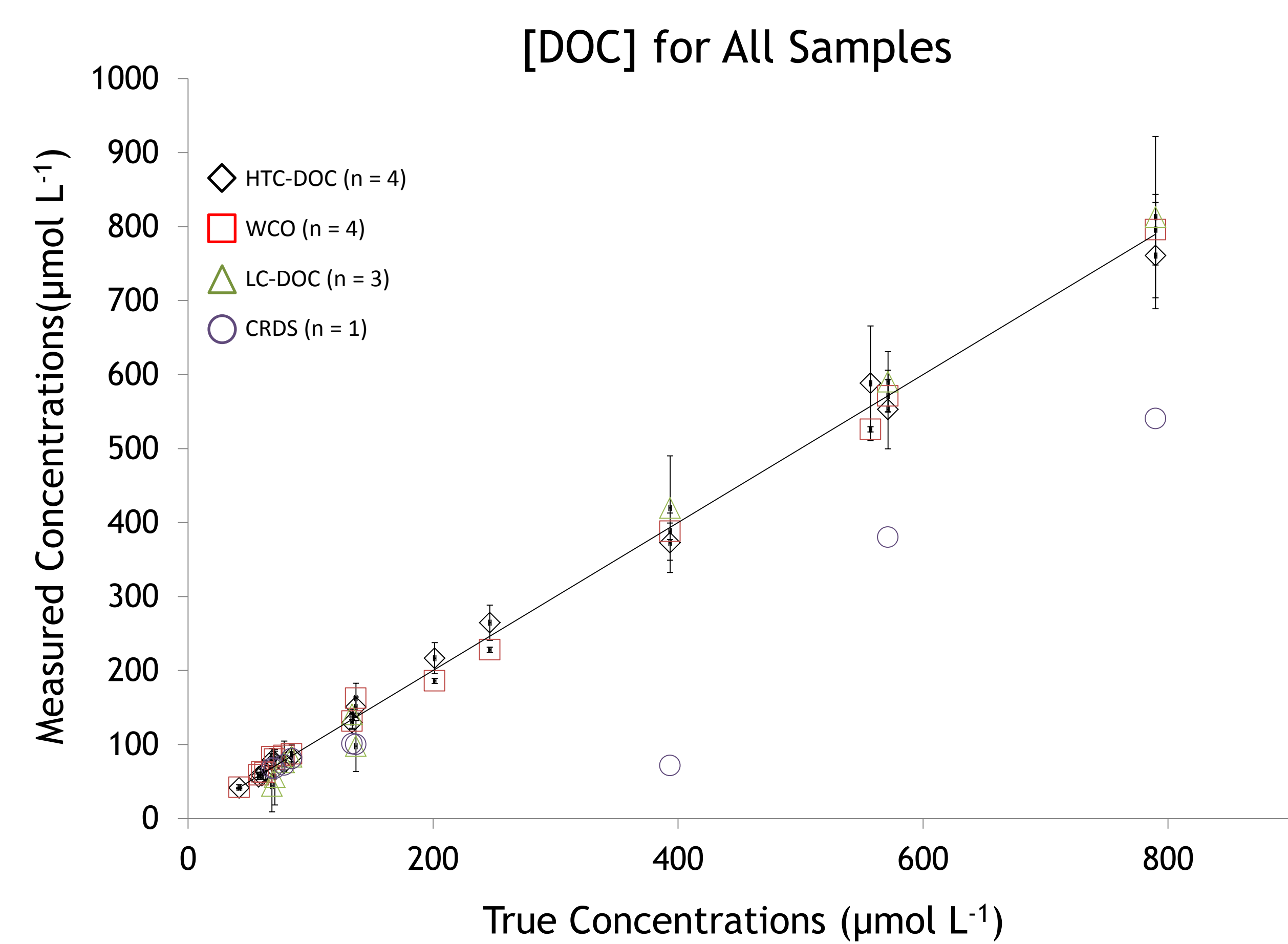


Figure 1 : Reported versus true (Solid line) of [DOC] measurements depending on oxidation method used

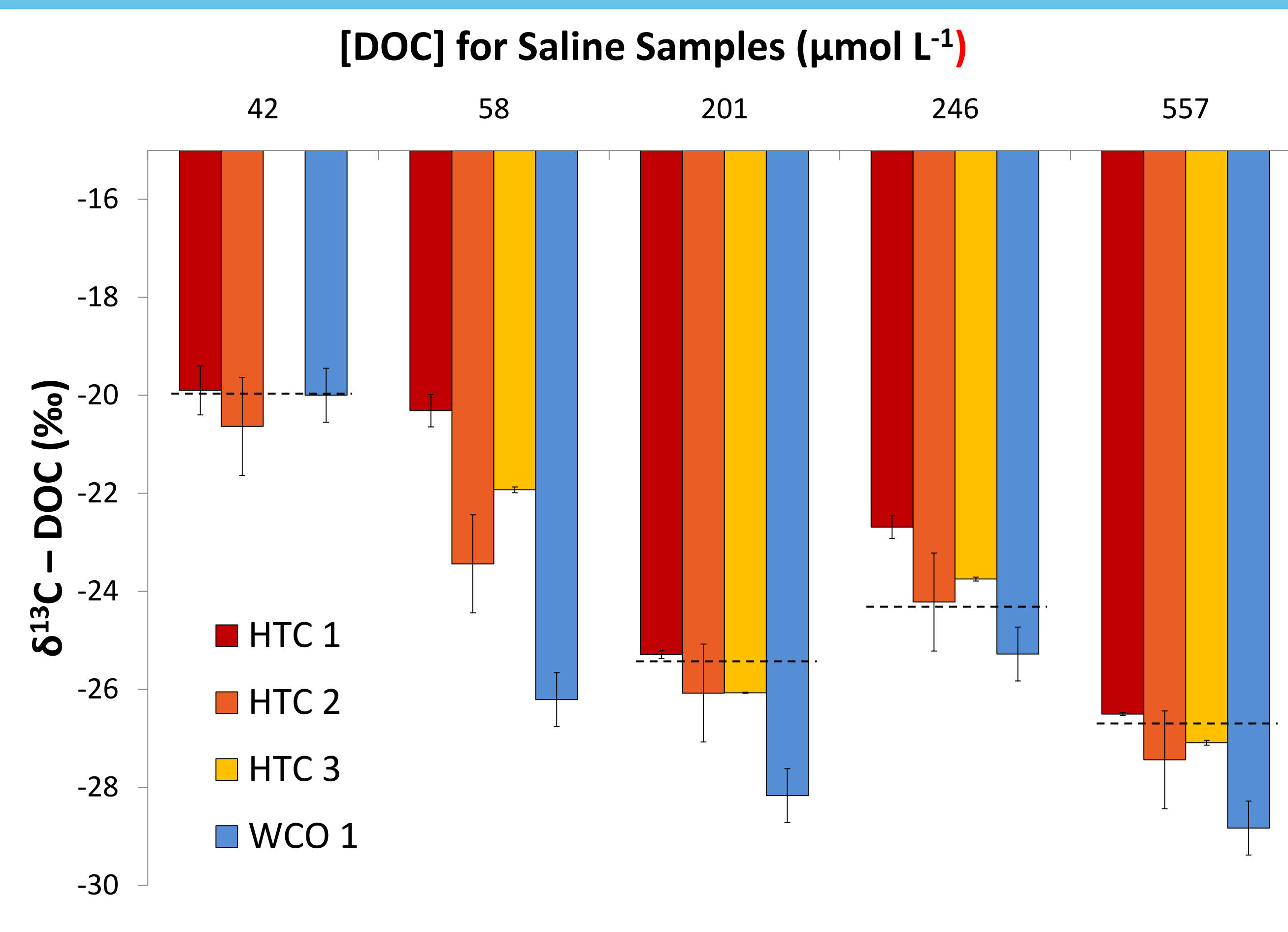


Figure 2 : $\delta^{13}\text{C}$ of saline solutions reported by various users (3 HTC-DOC users and 1 WCO user). Dotted lines represent "true" value, when available

A set of four Potassium Hydrogen Phthalate (KHP) solutions and 2 lake UDOM samples (known $\delta^{13}\text{C}$) with varying DOC concentrations were included in the sample set unbeknownst to the analysts.

Using these samples we can compare the ability of each oxidation method to measure the $\delta^{13}\text{C}$ -DOC of simple solutions at different concentrations

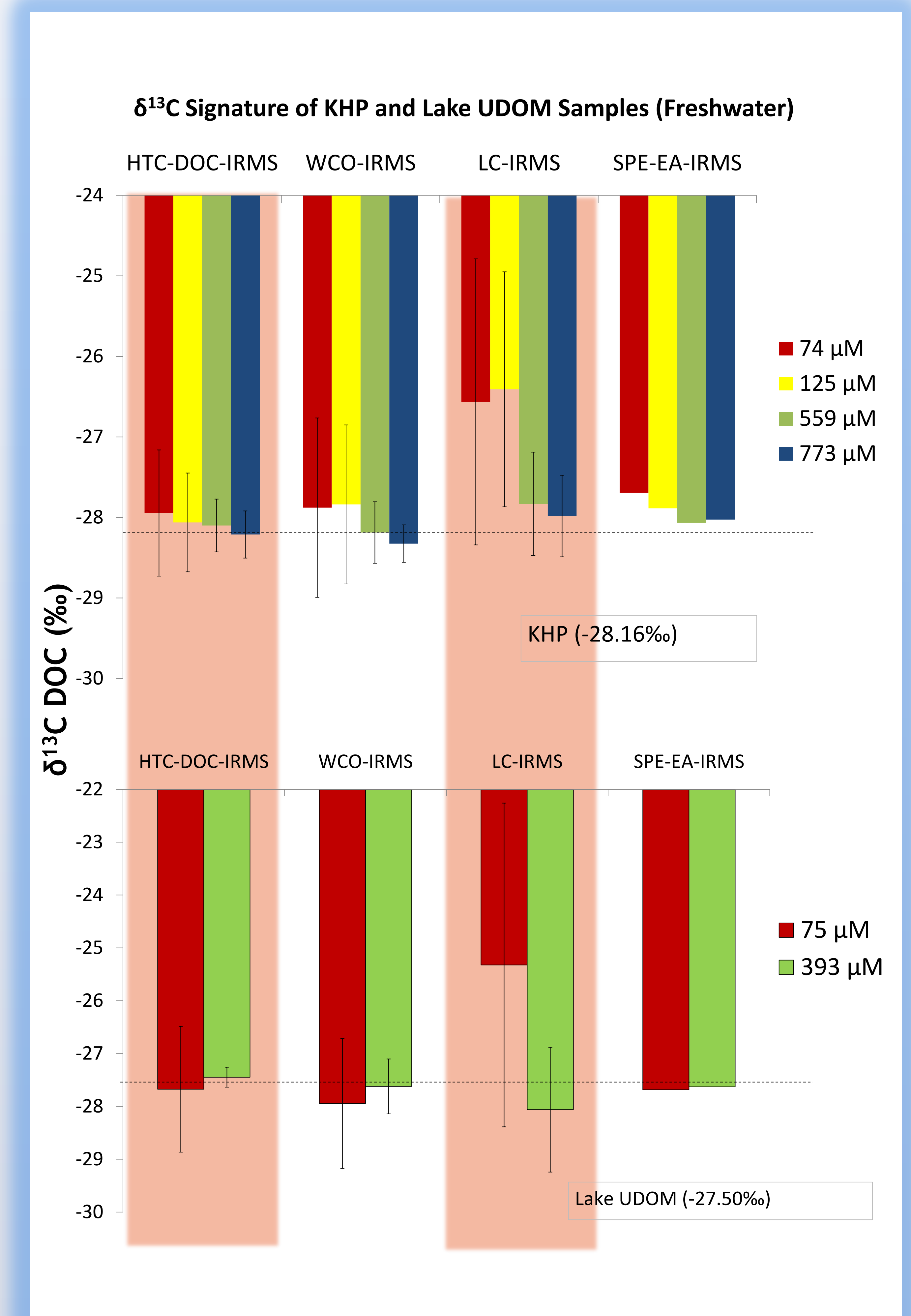


Figure 3 : Reported $\delta^{13}\text{C}$ of KHP solutions and Lake UDOM samples as a function of oxidation method and solution concentration (μM). True $\delta^{13}\text{C}$ values are shown as dotted lines

Conclusions & Recommendations

- [DOC] can be determined accurately for all methods but $\delta^{13}\text{C}$ remains a difficult measurement, especially for low [DOC] solutions;
- Salty solutions were not analyzed by most participants because of analytical limitations. Only 3 HTC instruments and 2 WCO instrument measured the $\delta^{13}\text{C}$ of the *total* DOC pool;
- Samples with mixed DOC sources (2 pools with very different $\delta^{13}\text{C}$ signatures) generated the highest standard deviations, possibly due to incomplete combustion of one of the DOC pools;
- Routine use of a complex natural sample with a known $\delta^{13}\text{C}$ signature is recommended to verify instrument performance.