

Recommendations and good practices for Dissolved Organic Carbon (DOC) analyses at low concentrations



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Objectives

An ISO [1] protocol for the determination of DOC exists since 2018, but it is certified for DOC values $\geq 1 \text{ mg L}^{-1}$, while many publications report DOC values much lower. This ISO protocol does not include indications on vials cleaning, filtering material, and type of caps and septa to be used.

- This study evaluates protocols for measurements of low DOC concentrations ($\leq 1 \text{ mg L}^{-1}$) in freshwaters.

Tests

- Vials:** brown (amber or opaque) glass *versus* plastic.
- Glass decontamination:** from 1h to 12h, at 450 °C or 500 °C.
- Filtration:** 0.45 μm CA, PTFE, PVDF, 0.7 μm GF/F, 0.22 μm PES.
- Acids:** HCl (p.a or Optima®), H_3PO_4 .
- Matrix effects :** $\Sigma\text{H}_2\text{S}$ (20 μM), Na^+ (0.13 M), Ca^{2+} (0.075 M).
- Storage:** pierced septa, acidification, 4°C *versus* -18 °C, up to 2 months.

Results

* R_{SB} = Ratio of the mean of sample blanks to machine blank DOC.
* RSD = Relative Standard Deviation.
* Filters: - 0.7 μm : glass fiber filters (GF/F),
- 0.45 μm : Cellulose Acetate (CA), hydrophilic polytetrafluoroethylene (PTFE), Sterivex® Polyvinylidene fluoride (PVDF),
- 0.22 μm : Sterivex® polyethersulfone (PES).
* UP water = ultra-pure water.

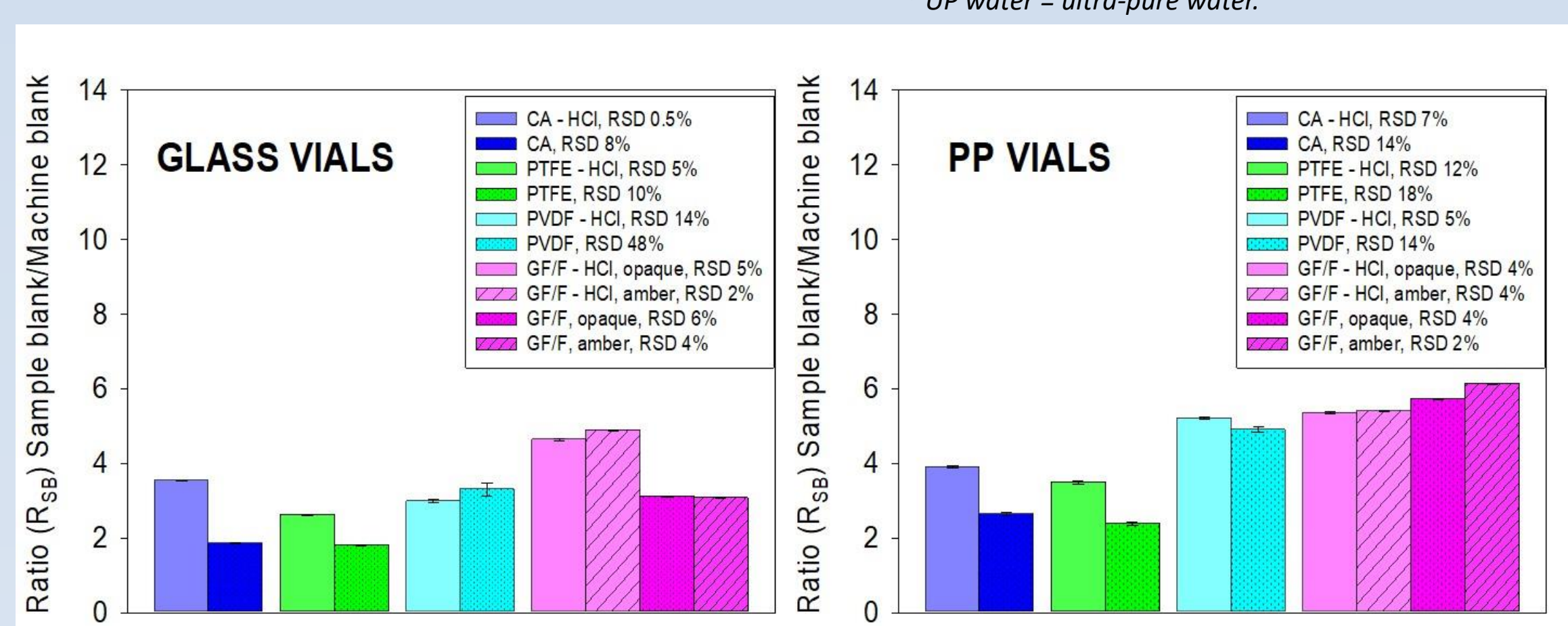


Fig.1. Sample blank = filtered UP water with or without HCl, stored in glass vials or in polypropylene (PP) vials. Filters: Cellulose Acetate (CA), hydrophilic Polytetrafluoroethylene (PTFE), glass fiber filters (GF/F), Polyvinylidene fluoride (PVDF). RSD calculated on duplicates.

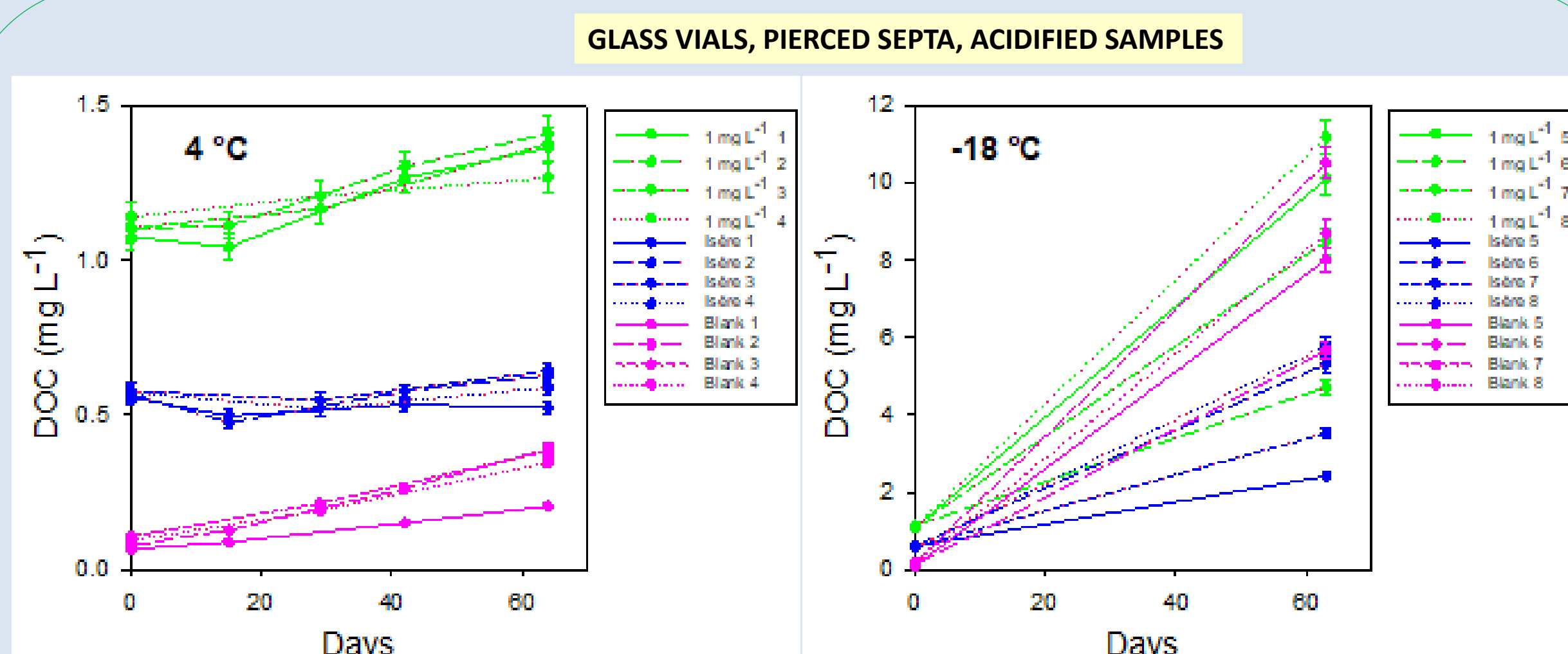


Fig.5. Monitoring of raw concentrations (i.e without blank subtracted to samples) of Isère River sample, 1 mg L⁻¹ DOC solution and blank of UP water stored in glass vials with pierced septa at 4 °C for 4 replicates (n°1 to 4) and at -18 °C for 4 other replicates (n°5 to 8).

WITH GLASS VIALS

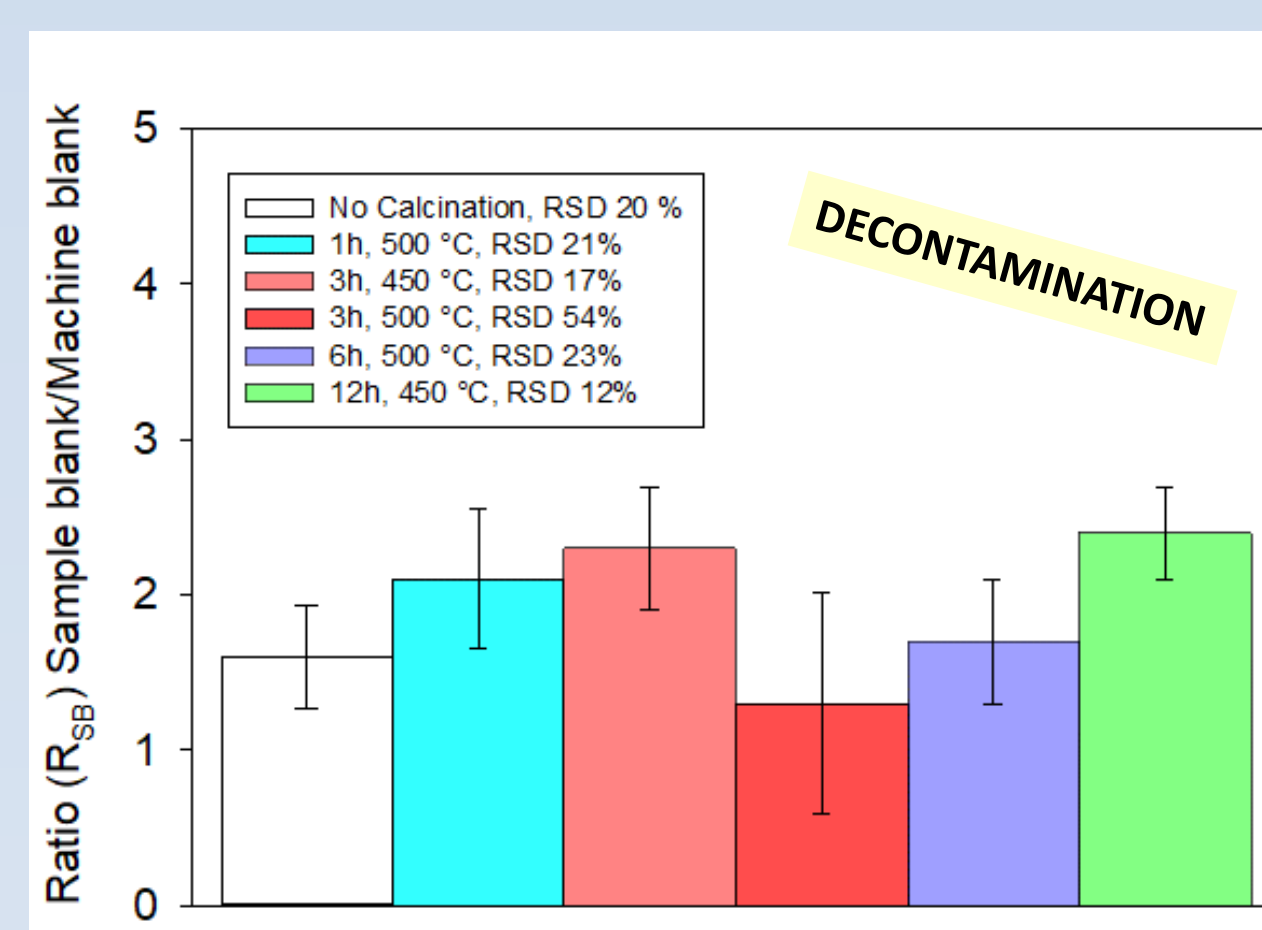


Fig.2. Sample blank = filtered UP water after contamination (citric acid 0.01M overnight) and decontamination of glass vials either with one UP water rinse, or coupled with a 450°C or 500°C calcination. RSD calculated on 10 replicates.

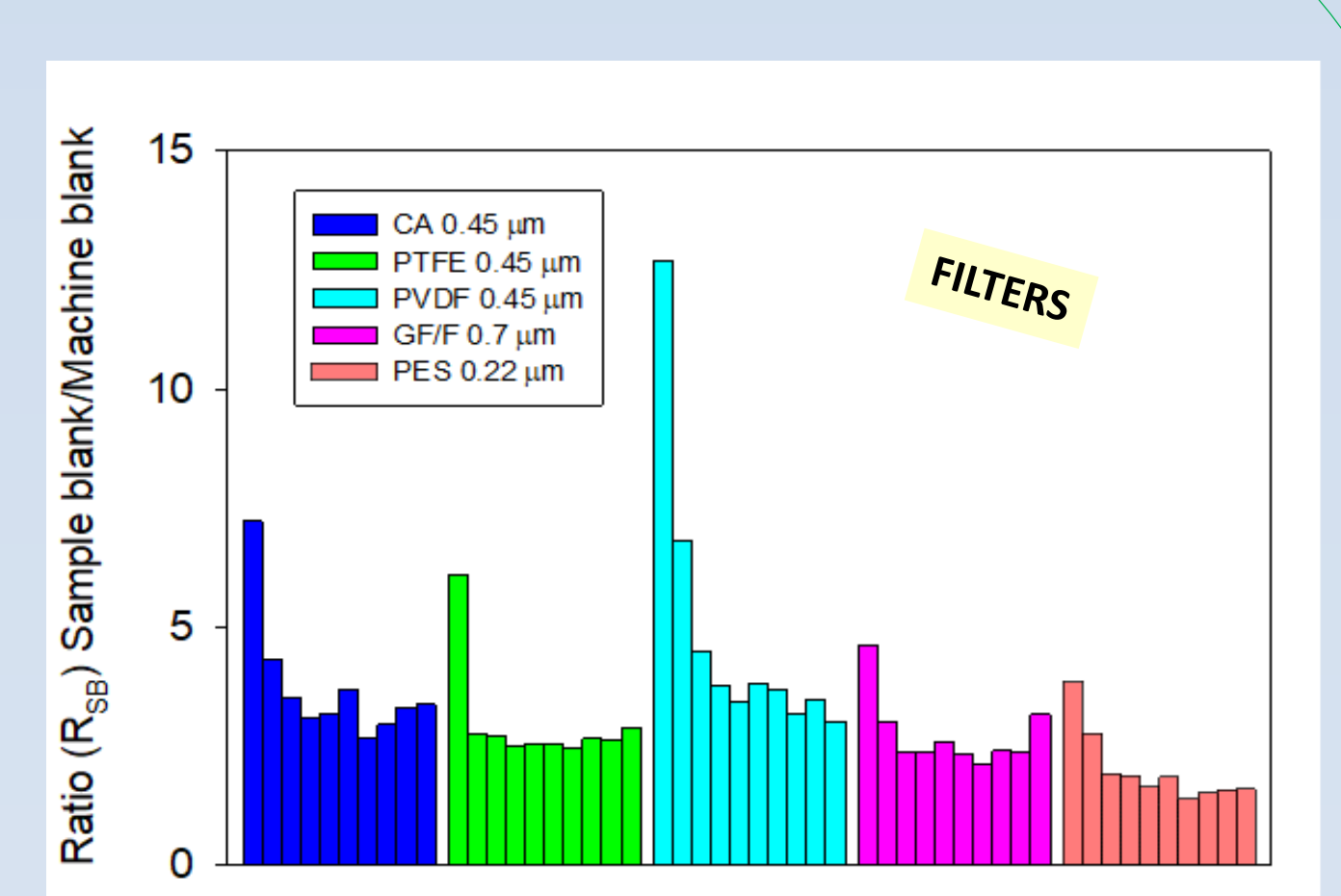


Fig.3. Sample blank = 20 ml of filtered UP water through CA, PTFE, Sterivex® PVDF, GF/F, Sterivex® PES for 10 successive filtrations using 20 ml of solution for each filtration step.

DOC (mg L ⁻¹)	Recovery % measured/theoretical value
UP Water	0.13
UP Water + HCl	0.21
UP Water + HCl + $\Sigma\text{H}_2\text{S}$	0.83
DOC 0.96 mg L ⁻¹	1.07
DOC 0.97 mg L ⁻¹ + HCl	1.11
DOC 0.96 mg L ⁻¹ + HCl + $\Sigma\text{H}_2\text{S}$	1.70
UP Water	0.12
UP Water + HCl	0.20
UP Water + HCl + $\Sigma\text{H}_2\text{S}$	0.71
DOC 1.13 mg L ⁻¹	1.25
DOC 1.01 mg L ⁻¹ + HCl	1.16
DOC 0.98 mg L ⁻¹ + HCl + $\Sigma\text{H}_2\text{S}$	1.67
UP Water + HCl + NaBr	0.20
DOC 1.03 mg L ⁻¹ + HCl + NaBr	1.16
DOC 1.06 mg L ⁻¹ + HCl + NaBr	1.15
UP Water + HCl + NaCl	0.34
DOC 1.02 mg L ⁻¹ + HCl + NaCl	1.27
DOC 1.06 mg L ⁻¹ + HCl + NaCl	1.31
UP Water + HCl + $\text{Ca}(\text{NO}_3)_2$	0.13
DOC 1.02 mg L ⁻¹ + HCl + $\text{Ca}(\text{NO}_3)_2$	1.07
DOC 1.01 mg L ⁻¹ + HCl + $\text{Ca}(\text{NO}_3)_2$	1.09

Table 1. Raw (i.e without sample blank subtracted to samples) DOC concentrations (mg L⁻¹), in the presence of HCl (0.5 ml of 0.3 vol% HCl per 20 ml [2]) and/or 20 $\mu\text{mol L}^{-1}$ $\Sigma\text{H}_2\text{S}$, or with (*) HCl diluted 10 times and sodium bromide (NaBr), or sodium chloride (NaCl) or calcium nitrate $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, with $[\text{Na}] = 0.13 \text{ mol L}^{-1}$ and $[\text{Ca}] = 0.075 \text{ mol L}^{-1}$. Sample blanks were subtracted to corresponding DOC sample for the calculation of Recovery %.

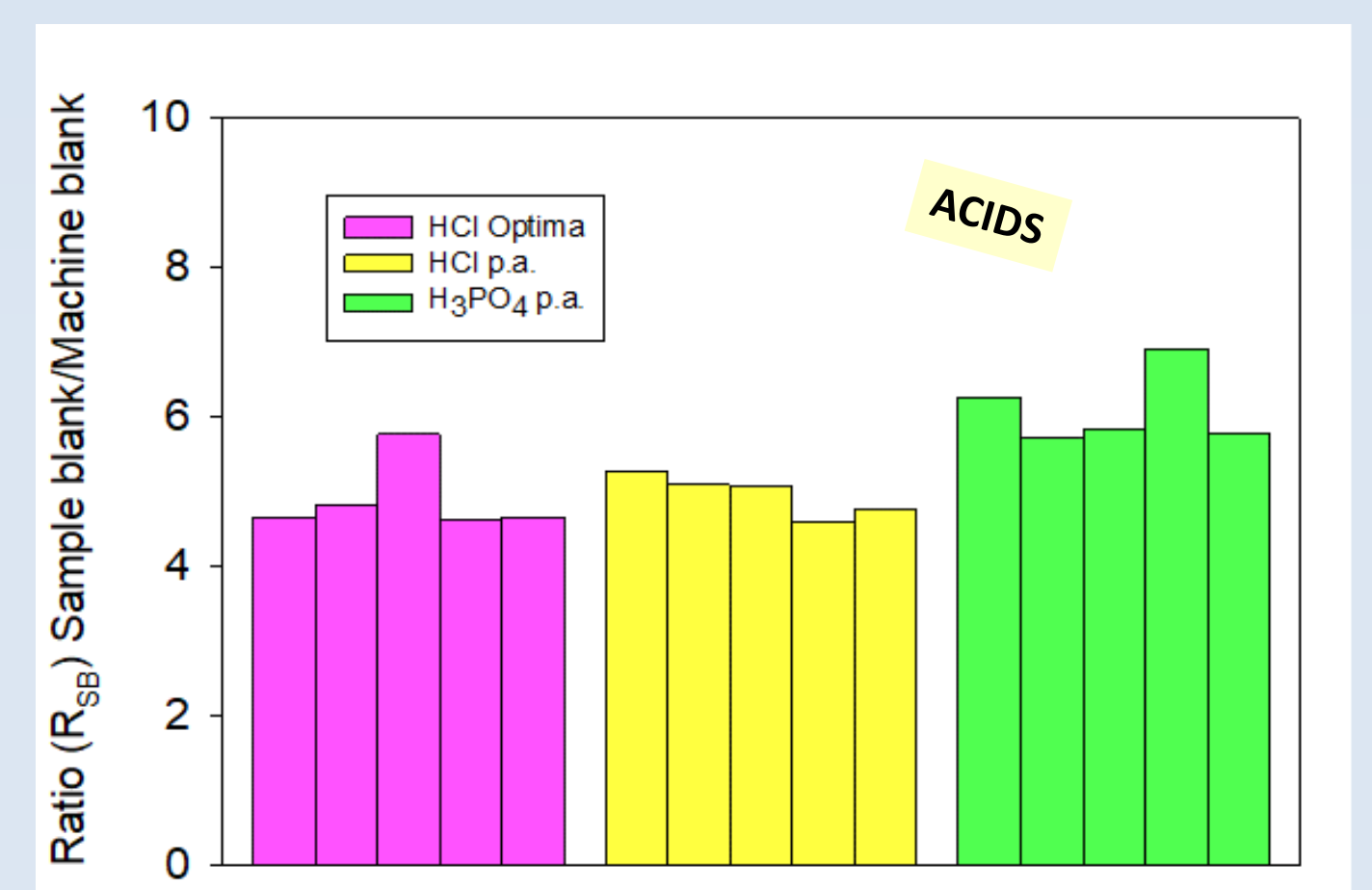
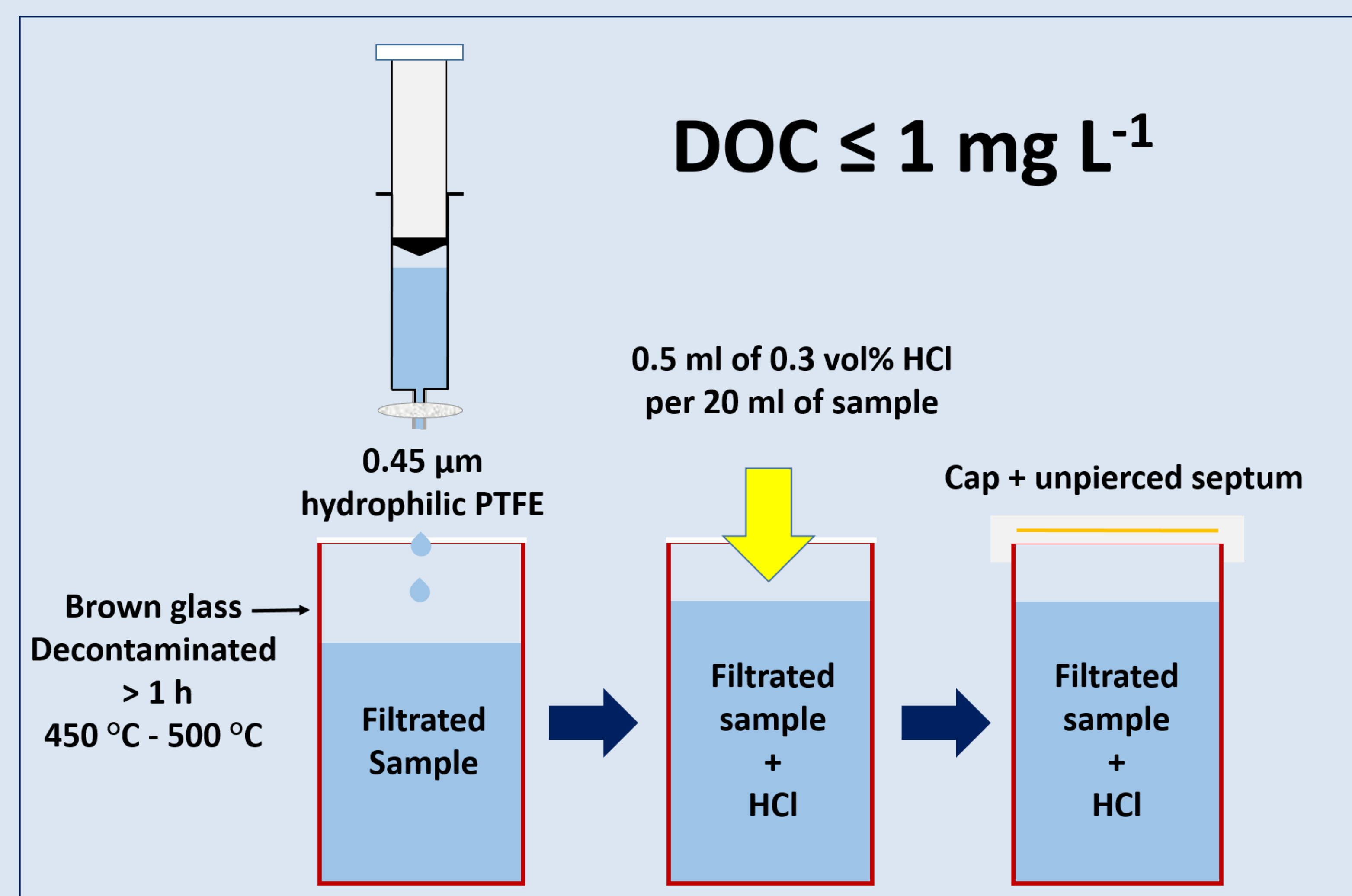


Fig.4. Sample blank = 20 ml of filtered UP water through PTFE, and acidified with Optima® HCl or analytical grade (p.a) HCl (0.5 ml of 0.3 vol% HCl [2]) or p.a. H_3PO_4 (670 μl of 2.5 vol% H_3PO_4 [3]). The five bars for each acid represent repetitions of the preparation.

Recommendations



- Amber or opaque 40 ml glass vials adaptable to autosampler, screwed PP caps, one-side PTFE septum.
- Pre-rinse filters with > 20ml (ultra-pure water or sample).
- Use 0.45 μm PTFE membrane.
- Use 0.7 μm GF/F if particule organic carbon is needed.
- Do sample blanks in the same conditions.
- Don't use pierced septa with sample acidification for sampling and storage.
- With unpierced septa PTFE-side, 40 ml glass vials for autosampler, acidification, screwed caps, store at room T °C up to 3 years [4].

References

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