

Poster Reprint

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# Strategies for Ultimate Sensitivity of Per- and Polyfluoroalkyl Substances (PFAS) in Water

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## Introduction

Per and polyfluorinated alkyl substances (PFAS) are a group of man-made compounds that are ubiquitous in environment. Possible adverse effects to humans and animals have made them a public health concern<sup>1</sup>. In June 2022, the USEPA issued interim drinking water health advisory limits (HALs) for PFOA at 0.004 ng/L, PFOS at 0.02 ng/L, GenX at 10 ng/L and PFBS at 2,000 ng/L to reduce the risk to the public from exposure to these PFAS<sup>1</sup>.

In March 2023, EPA proposed National Primary Drinking Water Regulation for six PFAS<sup>1</sup>, adding PFHxS and PFNA to the list covered in the HALs. The proposed maximum contaminant level (MCL) for both PFOA and PFOS was set to 4 ng/L, higher than the toxicologically based HALs. The remaining compounds are proposed to be covered by a Combined Hazard Index Calculation.

With the 3<sup>rd</sup> generation iFunnel technology (G6495C) we showed that with a large volume injection utilizing either a focusing guard cartridge or a sandwich injection that achieving the HAL values was possible when extracting per EPA 533<sup>2</sup>. However, background contamination is very problematic and usually exceeds the HAL value for PFOA.

While achieving the HAL level is not necessary, it is ideal to maintain sensitivity with routine implementation of EPA 533. Here we show what can be achieved with the 4<sup>th</sup> generation iFunnel technology on the new 6495 LC/TQ (G6495D) with a typical injection volume with comparison to the earlier model.



**Figure 1. Infinity II 1290 and 6495 LC/TQ and Agilent Bond Elut PFAS WAX SPE Cartridge.**

## Methods

A bottled drinking water, two different tap waters and reagent water blank were collected and extracted following US EPA Method 533<sup>3</sup> using the Agilent Bond Elut PFAS WAX SPE cartridge. Native PFAS standards and isotopically labeled analogues were purchased from Wellington Labs. Standards were diluted to the low pg/mL range to evaluate instrument sensitivity while using a routine injection volume for EPA 533 analysis. The native samples were evaluated to confirm sensitivity and background. The extracts and standards were in 80:20 methanol:water.

An intelligent source optimization algorithm (MassHunter Source Optimizer) was used to define the ideal source temperatures and conditions for EPA 533 target compounds. LC and instrument parameters are shown in Table 1.

### LOQ Determination

The LOQ determination required a peak S/N (> 10), reproducibility (< 20%), accuracy within 30% and a calibration fit with  $R^2 = 0.99$  and Relative Standard Error (RSE) < 20.

**Table 1. LC and 6495 LC/TQ Parameters**

Column	<ul style="list-style-type: none"> <li>Zorbax Eclipse Plus C18, 2.1 x 100mm, 1.8 <math>\mu</math>m</li> <li>PFC Delay Column, 4.6 x 30 mm</li> </ul>
Flow Rate	0.4 mL/min
Injection volume	3 $\mu$ L
Column Temperature	40 $^{\circ}$ C
Mobile Phase	A: 2 mM Ammonium Acetate in Water B: 95:5 Acetonitrile: water
Run time	12.5 minutes
Gas Temperature	150 $^{\circ}$ C
Gas flow	18 L/min
Nebulizer	25 psi
Sheath Gas Temperature	390 $^{\circ}$ C
Sheath Gas flow	18 L/min
Capillary Voltage	2500 V (ESI-)
Funnel voltages	Standard

## Results and Discussion

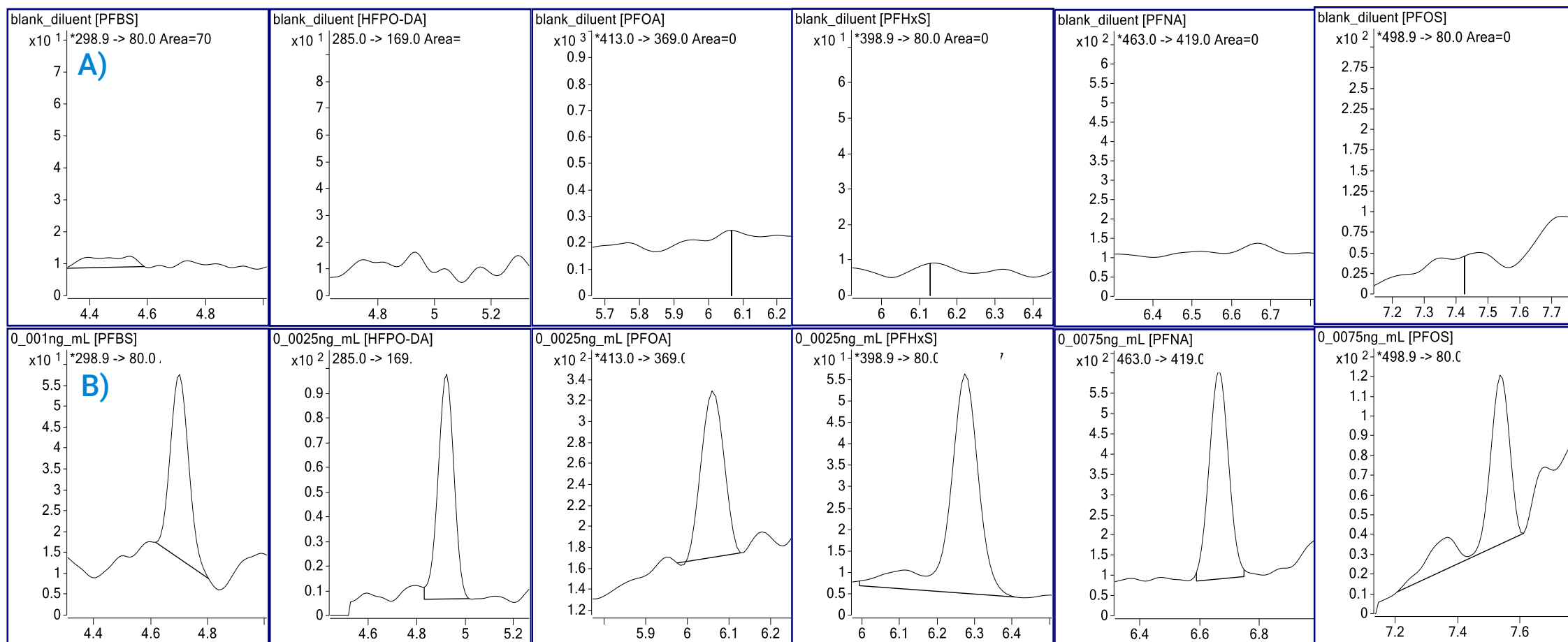


Figure 2. Chromatograms-A) Blank B) Compound Chromatograms at LOQ level (New 4<sup>th</sup> Generation 6495 LC/TQ (G6495D)). From Left, PFBS, HFPO-DA, PFOA, PFHxS, PFNA, and PFOS

Table 2. Concentration corrected Limit of Quantitation (LOQ) on Each Instrument Models

	3 <sup>rd</sup> Generation iFunnel LOQ (ng/L)	4 <sup>th</sup> Generation iFunnel LOQ (ng/L)
PFBS	0.01	0.004
HFPO-DA	0.01	0.01
PFOA	0.02	0.01
PFHxS	0.02	0.01
PFNA	0.03	0.03
PFOS	0.2	0.03

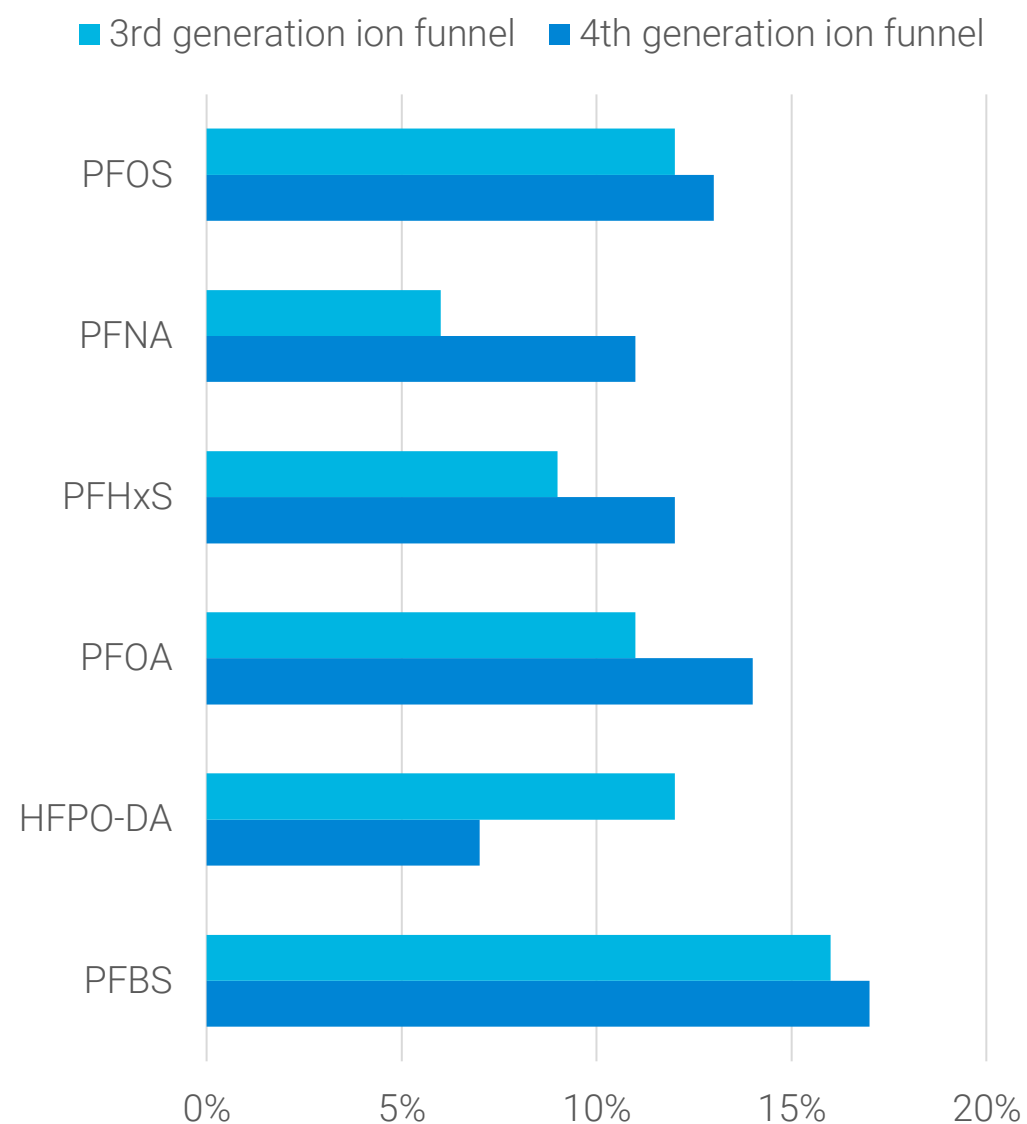
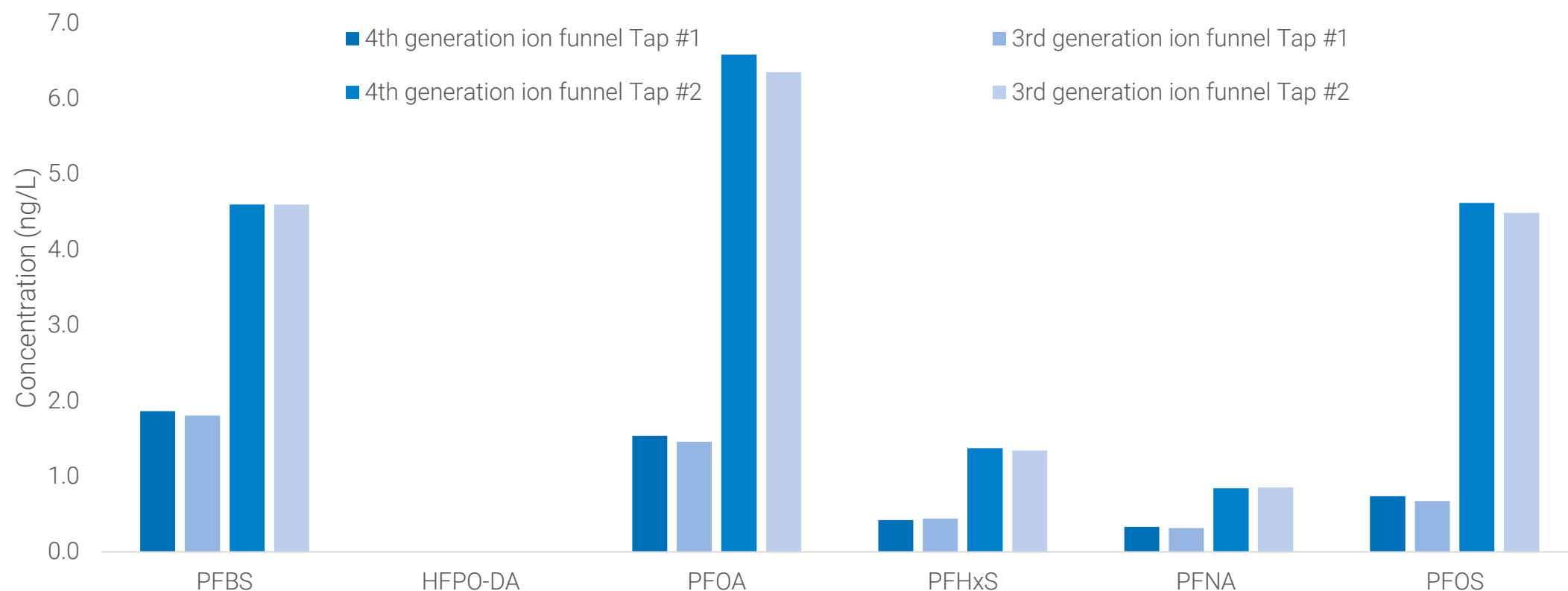


Figure 3. RSD (n=8) at LOQ Level for Both Instrument Models

## Results and Discussion



**Figure 4. Concentration in Water Samples. No MCL compounds were detected in method blank or bottled water sample**

### MS Resolution Width

The 6495 LC/TQ offers a “narrow” (0.4) isolation width as a compound setting. During method development a large interfering peak was noticed for PFHxA at low concentration levels. Updating the isolation width to narrow removed the interference (Figure 5). While still allowing sensitive performance within the calibration range.

### Results

The 4<sup>th</sup> generation iFunnel showed improved performance with a 2.5 – 7x increase in sensitivity. The increase was compound dependent with PFOS showing the greatest increase.

Extracted water samples concentrations analyzed separately on both the 6495 LC/TQ and its predecessor were comparable. The bottled water sample and method blank sample did not contain any significant level of the MCL compounds. While the both tap water samples showed detectable levels of 5/6 compounds.

### Conclusions

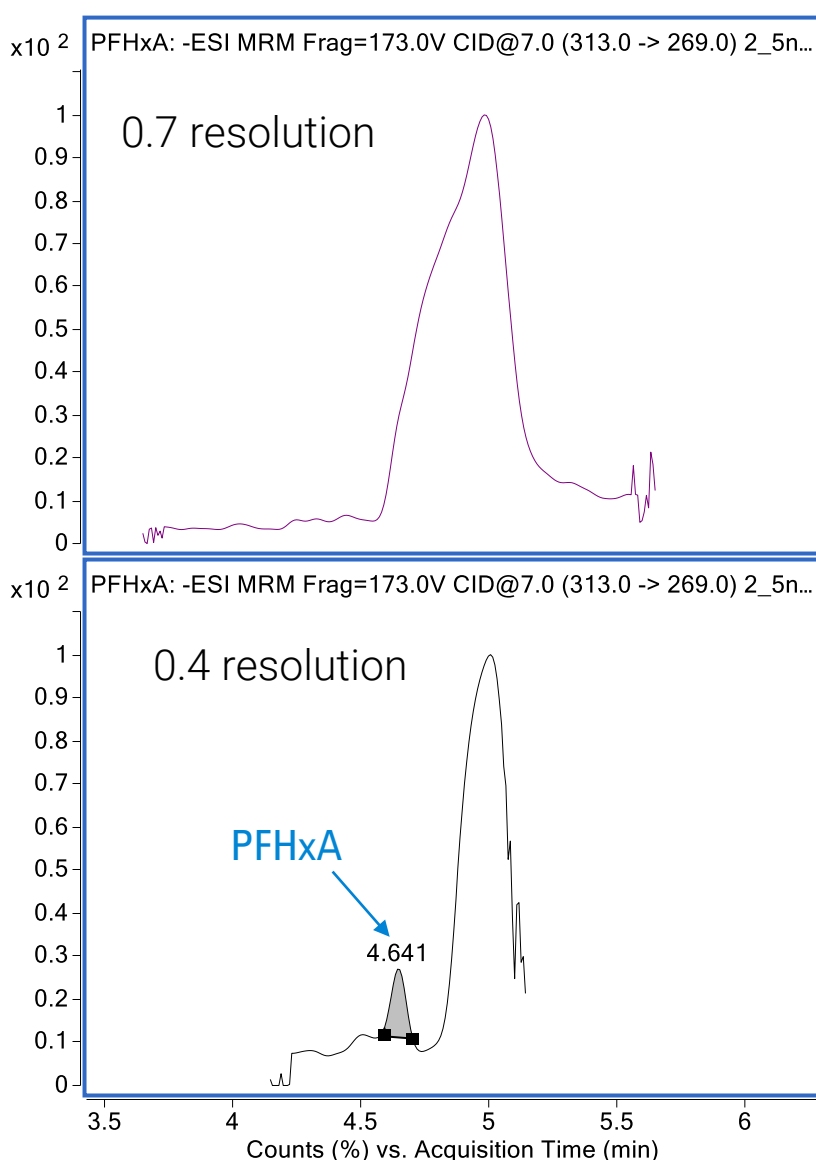
- The 4<sup>th</sup> generation iFunnel showed improved performance with a 2.5 – 7x increase in sensitivity for the 6 MCL PFAS compounds.
- Narrow MS Resolution removed an interference at low concentrations.

### References

<sup>1</sup>United States Environmental Protection Agency, Per- and Polyfluoroalkyl Substances (PFAS). <https://www.epa.gov/pfas> (accessed May 4, 2023).

<sup>2</sup>Ultra-Trace Quantification of Per- and Polyfluoroalkyl Substances (PFAS) in Drinking Water. Agilent Technologies application note, publication number 5994-5797EN.

<sup>3</sup>Method 533: Determination of Per and Polyfluoroalkyl Substances in Drinking Water by Isotope Dilution Anion Exchange Solid Phase Extraction and Liquid Chromatography/Tandem Mass Spectrometry. USEPA Office of Water 2019.



**Figure 5. Narrow MS Resolution Width Removed PFHxA Interference at Low Concentrations**

<https://www.agilent.com/en/promotions/asms>

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