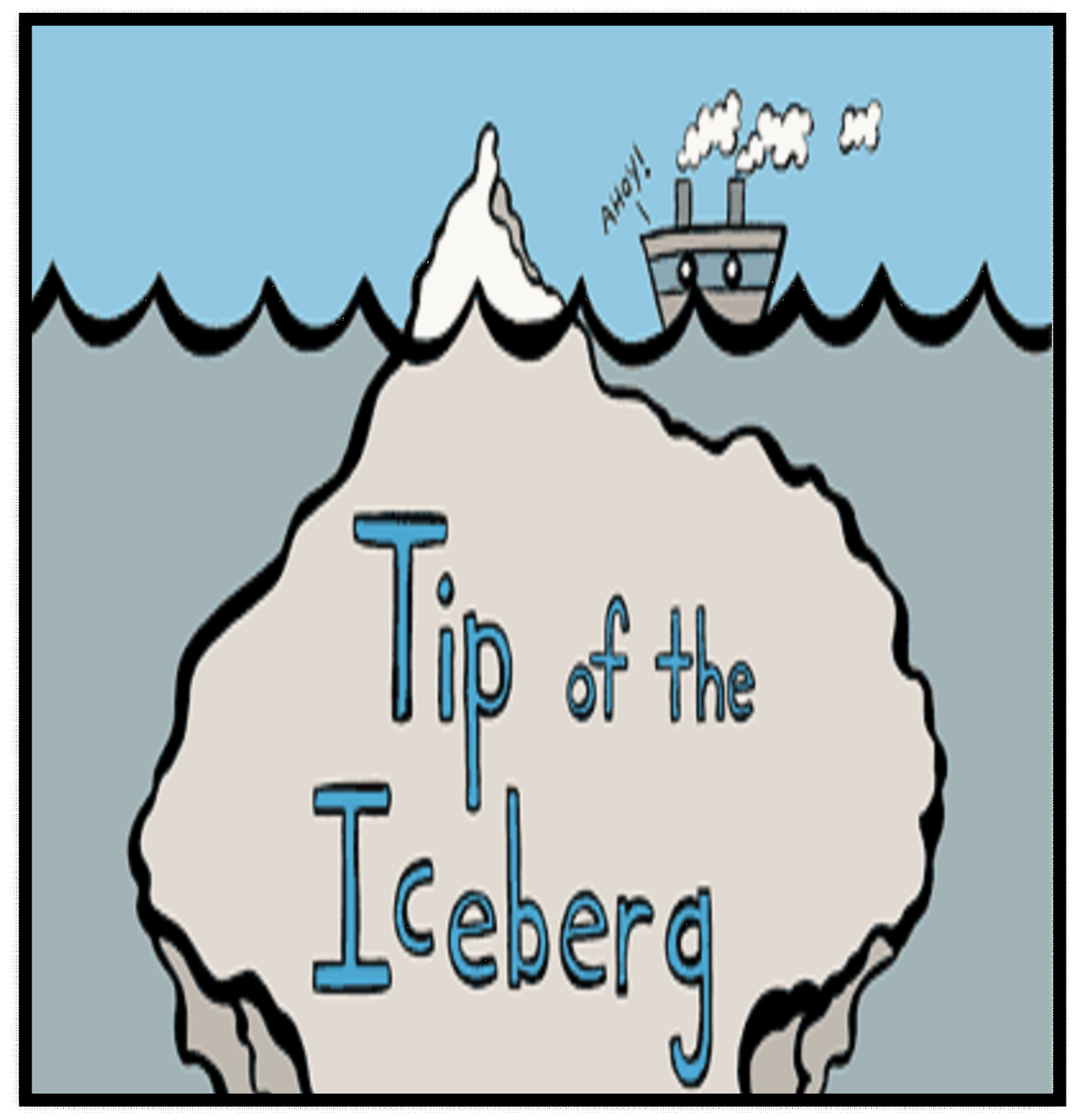
TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

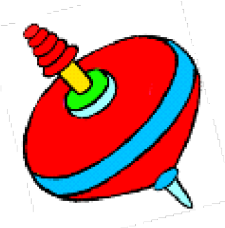
# Closing the PFAS Mass Balance: The Total Oxidizable Precursor (TOP) Assay

Karla Buechler, TestAmerica Laboratories, Inc.

## EXECUTIVE SUMMARY

Current methodologies for the analysis of per and polyfluoroalkyl substances (PFAS) are designed to measure a discrete list of 14 to 30 compounds. There are many additional PFAS compounds that are not determined as discrete compounds by existing analytical methods, including Method 537. Hence, we may be underestimating the PFAS transformation potential present in the environment. There is significant pressure from the public, environmental agencies, and others to apply methodologies that more closely measure the full extent of PFAS contamination. A new method, the Total Oxidizable Precursor (TOP) assay, can help measure the concentration of non-discrete and difficult to measure PFAS compounds that are not determined by conventional analytical methods. Assessment of TOP assay data may improve our understanding of potential PFAS environmental risk (Figure 1).





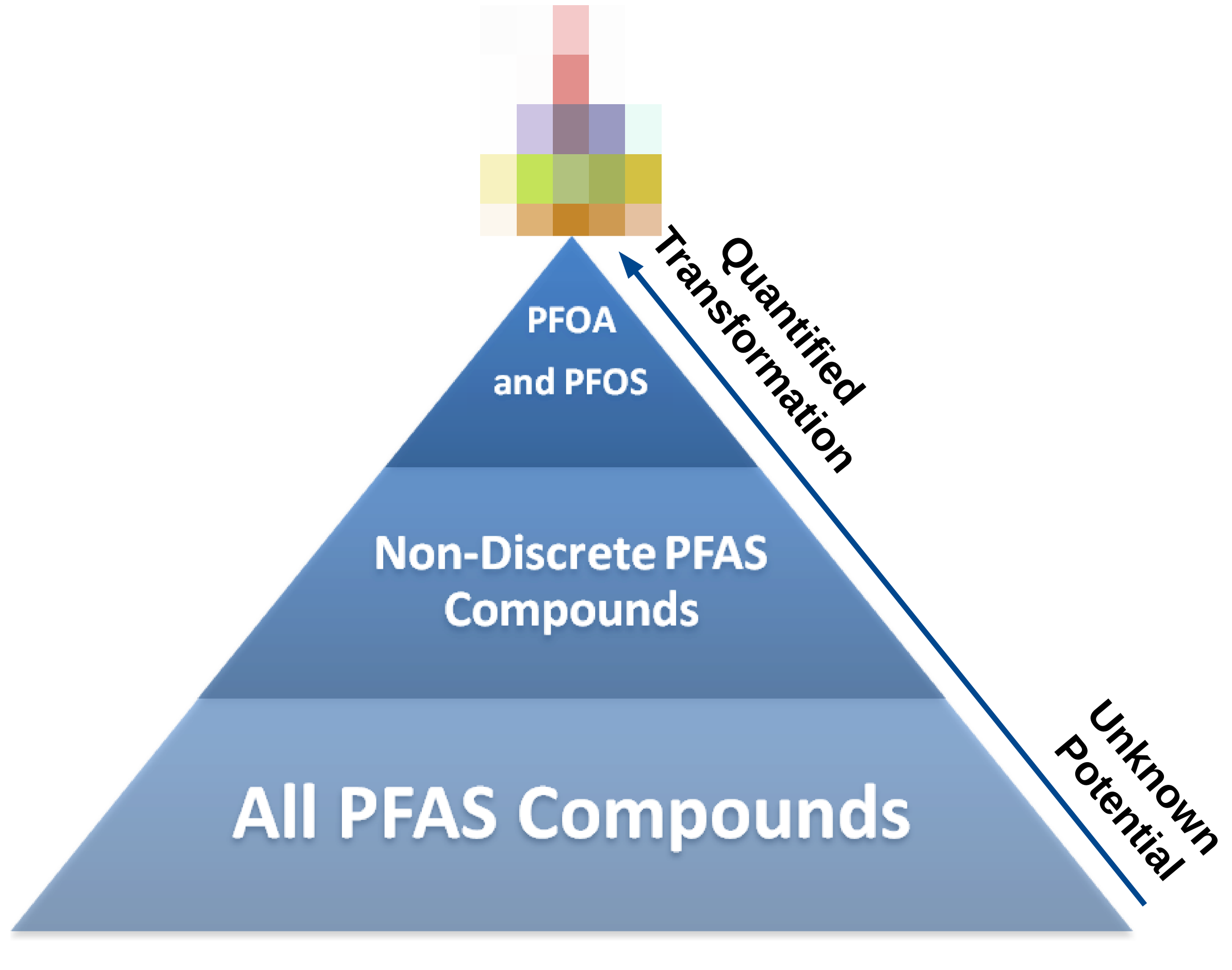
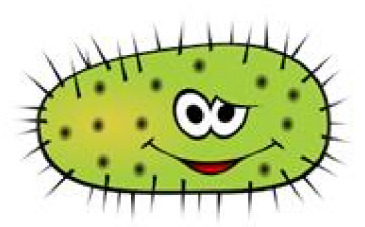


Figure 1: Potential PFAS Risk

## BACKGROUND

PFAS are a family of hundreds of synthetic compounds used in a wide variety of industrial and commercial products such as textiles, leathers, aqueous film forming foams (AFFF), metal plating, photo lithography, semi-conductors, paper and food packaging, coating additives, cleaning products and pesticides. Each contains carbon (C) chains with fluorine (F) atoms attached to these chains. The C-F bond is the shortest and strongest bond in nature, and is responsible for most of the unique and useful characteristics of these compounds. PFAS include perfluorinated sulfonic acids (i.e. PFOS) and perfluorinated carboxylic acids (i.e. PFOA). PFOS and PFOA are fully fluorinated organic compounds and were the most common PFAS compounds produced in the United States. All PFAS are emerging contaminants of concern because they are persistent, and some forms are bioaccumulative. They are found widely in the environment and in human blood.



Polyfluorinated compounds are often referred to as "precursors" to the perfluoroalkyl acids (PFAAs), as they biotransform to PFAAs as dead end environmental products (Figure 2).

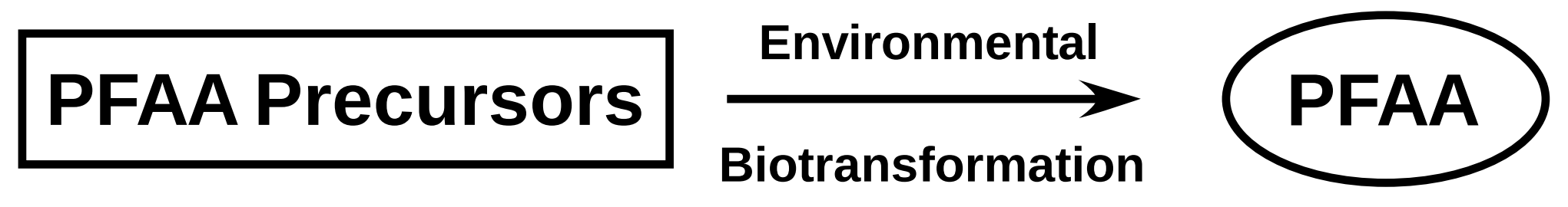


Figure 2: PFAA Precursors

An example of these environmental biotransformation processes is often seen in biological waste water treatment plants, where significantly more PFOA and PFOS are measured at the outflow than the inflow (Figure 3). The increase is explained by the fact that many PFAS compounds enter the sewage treatment plant uncharacterized and are biotransformed to PFAAs of various chain lengths with PFOS and PFOA often being the only analytes assessed.

Figure 3: Biotransformation

## CURRENT ISSUE

**How can we quantify this potential for PFAA production?**
Current commercially available analytical methodologies are not capable of quantifying the full suite of PFAS compounds that exist in soil and groundwater. Many PFAS compounds in the soil and groundwater will progress through a biotransformation funnel that leads to PFAAs as dead-end daughter products. This presents a significant analytical chemistry challenge.

The commercially available analytical PFAS method for finished drinking water is EPA Method 537. A modification (M) to Method 537 is used for more complex matrices. Both methods employ liquid chromatography with tandem mass spectrometry (LCMSMS) to quantify a suite of 20 to 30 PFAS. The reporting limits for Methods 537 and 537M range from 2 parts per trillion (ppt) to 40 ppt. These reporting limits are capable of achieving the EPA's provisional health advisory level of 70 ppt for PFOS and PFOA. However, these methods are not currently designed to identify and report the results of the full suite of PFAS. For example, the fluorotelomers and the many other PFAS compounds that biotransform are left undetermined. In order to fully understand the potential extent of PFAS in the environment, additional laboratory techniques are needed.

TestAmerica Sacramento implemented the TOP assay as a solution to this complex problem. The TOP assay rapidly converts polyfluorinated PFAA precursors into PFAAs including PFOA, using a hydroxyl radical-based chemical oxidation method. The oxidation reaction is detailed in Figure 4. The TOP assay replicates what micro-organisms in the environment would achieve after many years. The end result is to provide a range of PFAAs which are detectable by LCMSMS (Figure 5). The TOP assay quantifies the sum of PFAS that could be converted to PFAAs in the environment. The TOP methodology has revealed that for AFFF-impacted sites, the existing analytical LCMSMS methods are only detecting an estimated 30% to 50% of the total PFAA mass present as PFAA precursors.

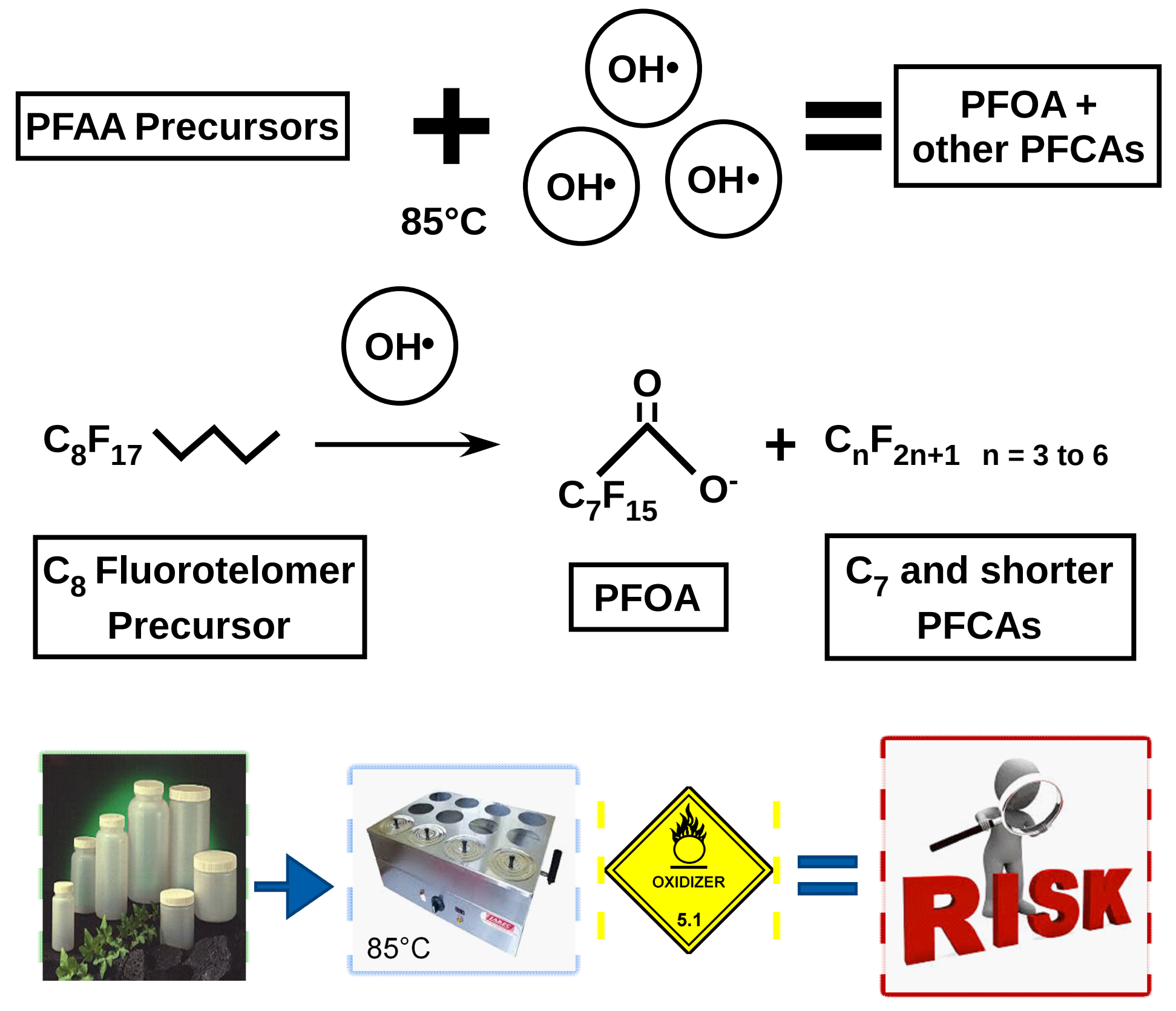


Figure 4: TOP Assay Chemical Reaction

1) Erika F. Houtz and David L. Sedlak, "Oxidative Conversion as a Means of Detecting Precursors to Perfluoroalkyl Acids in Urban Runoff," Environmental Science and Technology 46, no. 17 (2012): 9342-49.

## RESULTS

The TOP assay chemistry is fairly straight forward. The source of hydroxyl radicals used in the oxidation of PFAA precursors is a combination of potassium persulfate and sodium hydroxide.
These oxidation reagents are added to the aqueous samples in 125 ml high density polyethylene (HDPE) containers. The assay containers are placed in a heated water bath for several hours. The oxidation is quenched and the post-treatment assay aliquots are ready for solid phase extraction and LCMSMS analysis per Method 537M.

Quantitation of both a pre-treatment (Pre-TOP) sample aliquot and a post-treatment (Post-TOP) sample aliquot is required (Figure 5). The difference between the Pre-TOP concentrations and the Post-TOP concentrations is the concentration of the non-discrete oxidizable PFAA precursors.

In figure 5, the PFAA precursors in the top half of the table have Pre-TOP concentrations ranging from 19 ppt for EtFOSAA to 33 ppt for FOSA. All five precursors are non-detect (ND) at 5 ppt in the Post-TOP aliquot. Therefore, the precursors are completely oxidized to form PFAAs, including PFOA. Additionally, the bottom half of the table in figure 5 shows the increase in concentration of the discrete PFAS compounds. In the Pre-TOP aliquots, the PFCA concentrations range from 23 ppt for PFHpA and 26 ppt for PFHxA. In the Post-TOP aliquots, all PFCA concentrations increase. The most significant increase is observed for PFOA with a Post-TOP concentration of 59 ppt.

| Precursor | Pre - TOP | Post - TOP | % Oxidation |
|---|---|---|---|
| FOSA | 32.68 | ND | 100% |
| MeFOSAA | 19.38 | ND | 100% |
| EtFOSAA | 18.83 | ND | 100% |
| 6:2 FTS | 31.69 | ND | 100% |
| 8:2 FTS | 26.37 | ND | 100% |
| **PFCA** | **Pre – TOP** | **Post - TOP** | **Total** |
| PFBA | 24.94 | 27.16 | 109% |
| PFPeA | 23.38 | 28.55 | 122% |
| PFHxA | 26.49 | 34.87 | 132% |
| PFHpA | 23.10 | 25.14 | 109% |
| PFOA | 23.72 | 58.71 | 248% |
|  | Total 122 | Total 174 |  |

Figure 5: The TOP Assay Data

The chromatographic results of post-treatment aliquots of laboratory spiked control samples are shown in the following charts. In chart 1 the aliquot is spiked with Me-FOSA only. PFOA is the dominate PFCA, with a smattering of others. In chart 2 the aliquot was spiked with 8:2 FTS only and the resultant pattern of PFCAs is very different from Me-FOSA. The dominant PFCA is PFHpA. Lastly, chart 3 represents the pattern of PFCAs that are present when the laboratory aliquots are spiked with 8 PFAA precursors. Again, PFOA is the predominate compound determined.

Karla Buechler, Corporate Technical Director for TestAmerica, is based in Sacramento, California. Karla has more than 30 years of experience in the environmental testing industry, including years of hands-on experience with Liquid Chromatography Mass Spectrometry and High Resolution Mass Spectrometry. Karla can be contacted at Karla.Buechler@testamericainc.com.

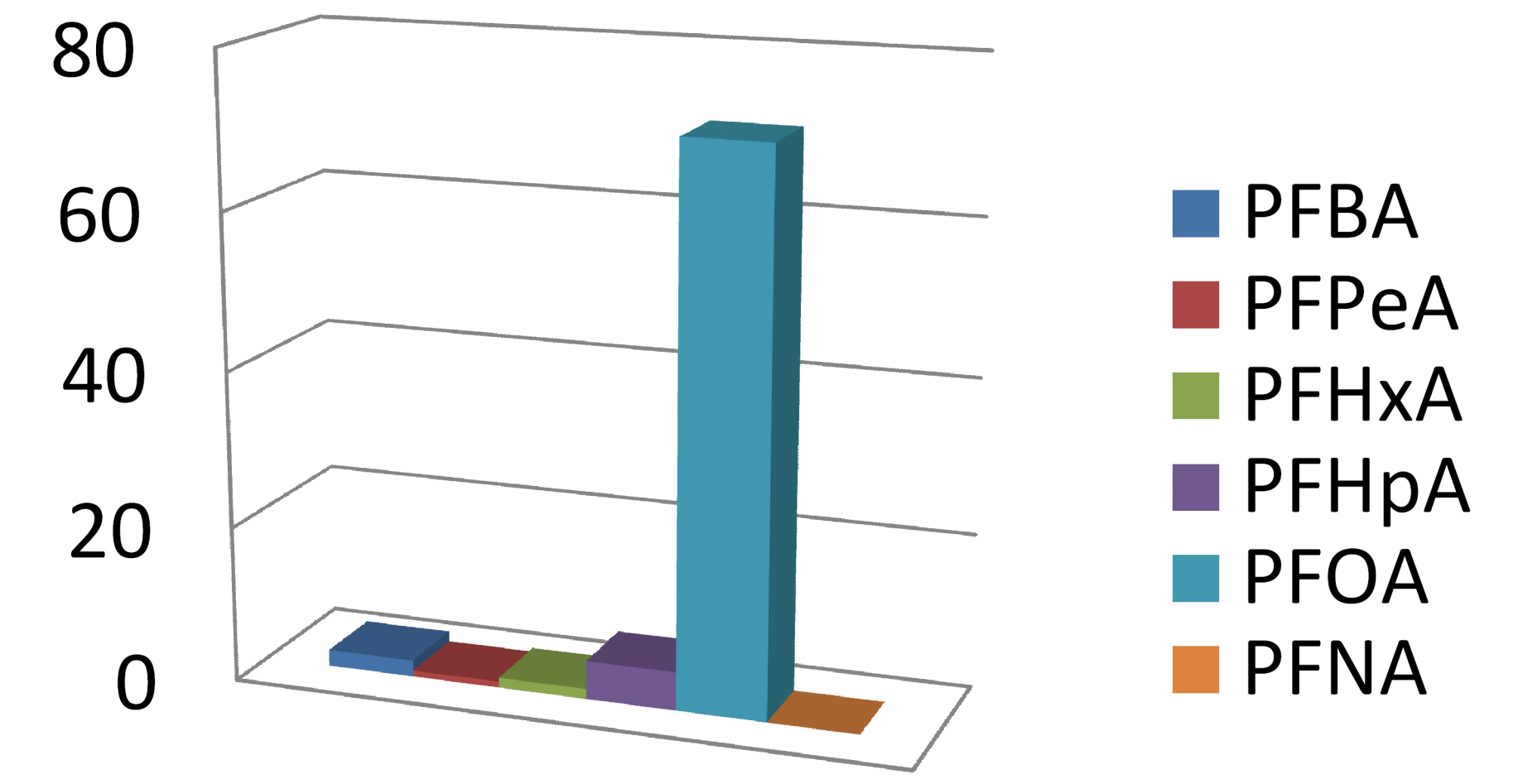


Chart 1: Precursor Me-FOSA

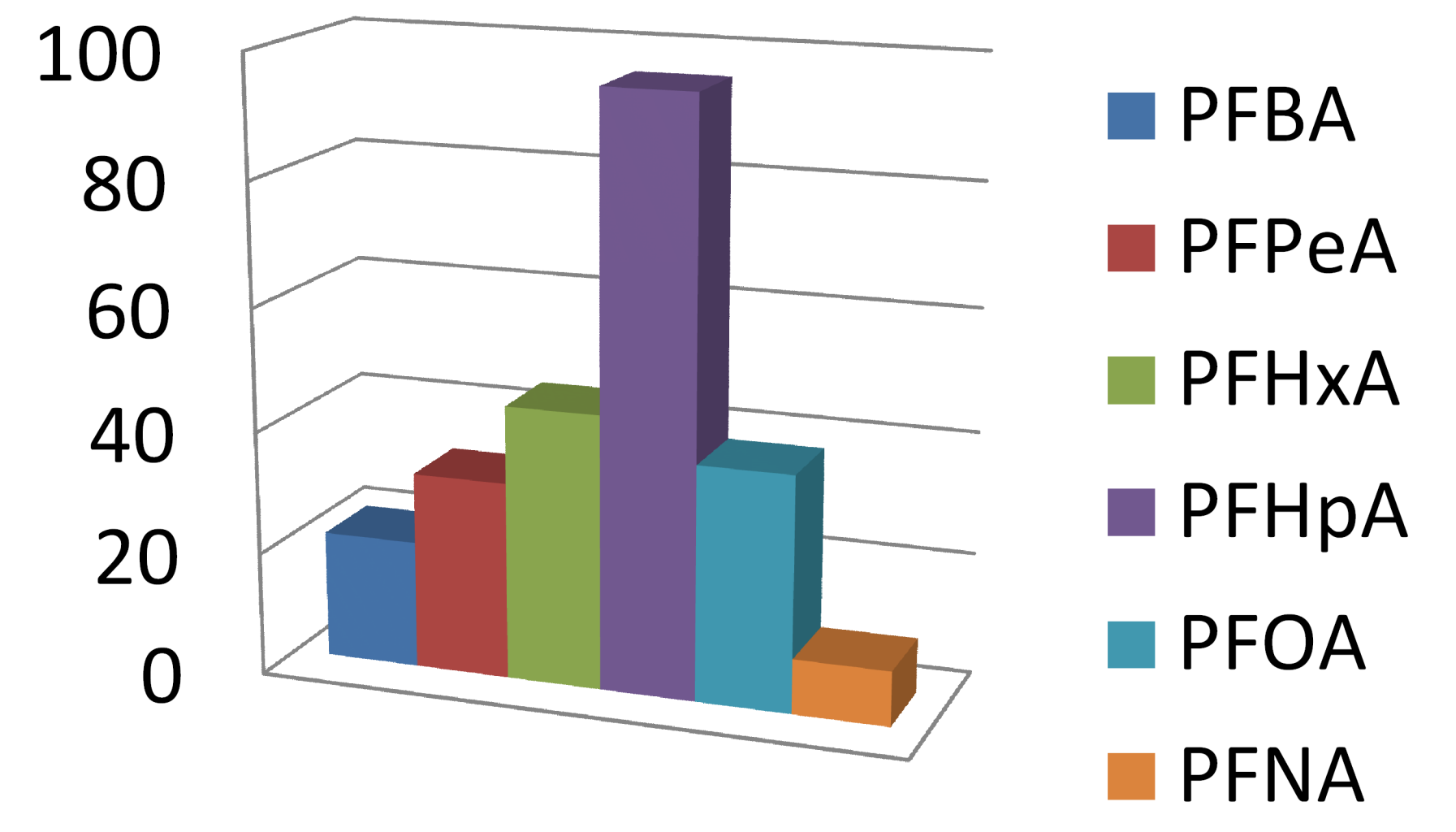


Chart 2: Precursor 8:2 FTS

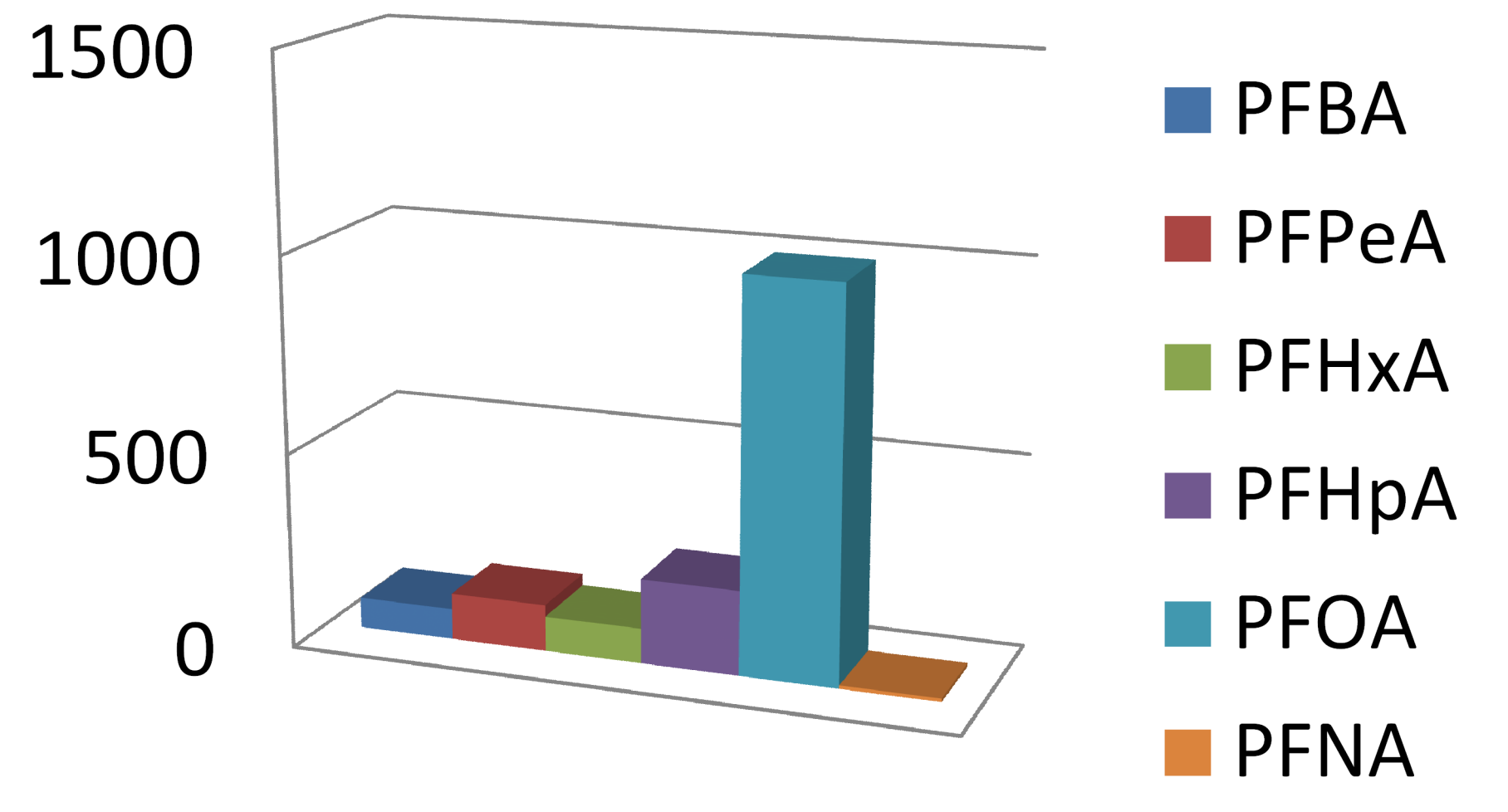


Chart 3: Sum of Precursors

## CONCLUSION

TOP assay data can help us understand the potential PFAS risk and it can provide valuable details regarding the carbon chain lengths of the PFAA precursors present at a site. There are also some limitations. Current analytical methods do not include all PFCAs; therefore, not all end products are determined and included in our potential PFAS risk evaluation. In addition, PFCA concentrations are not molar corrected, so the TOP analytical results do not depict a mass balanced equation.