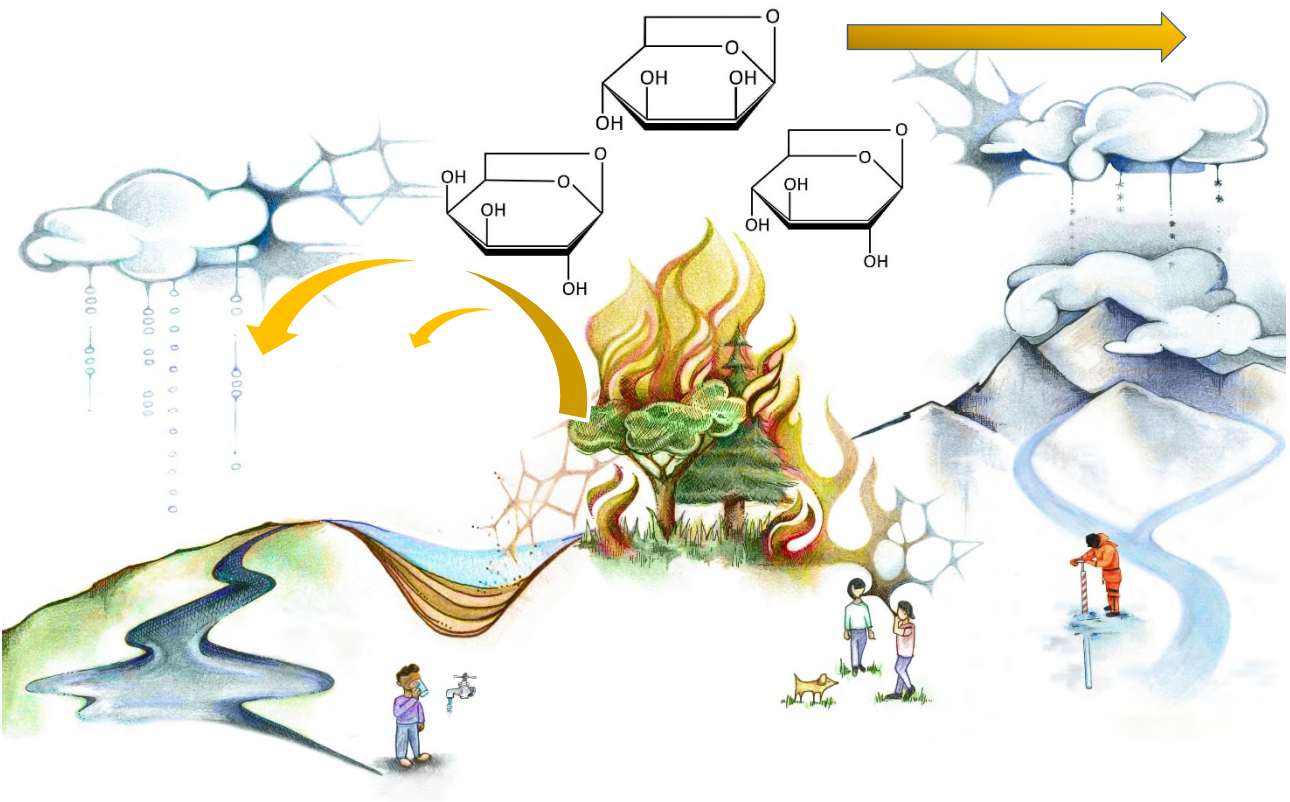
11th National Monitoring Conference
March 28, 2019

Monitoring Impacts of Wildfires on Air and Water Quality by Using Monosaccharide Anhydride Tracer Molecules



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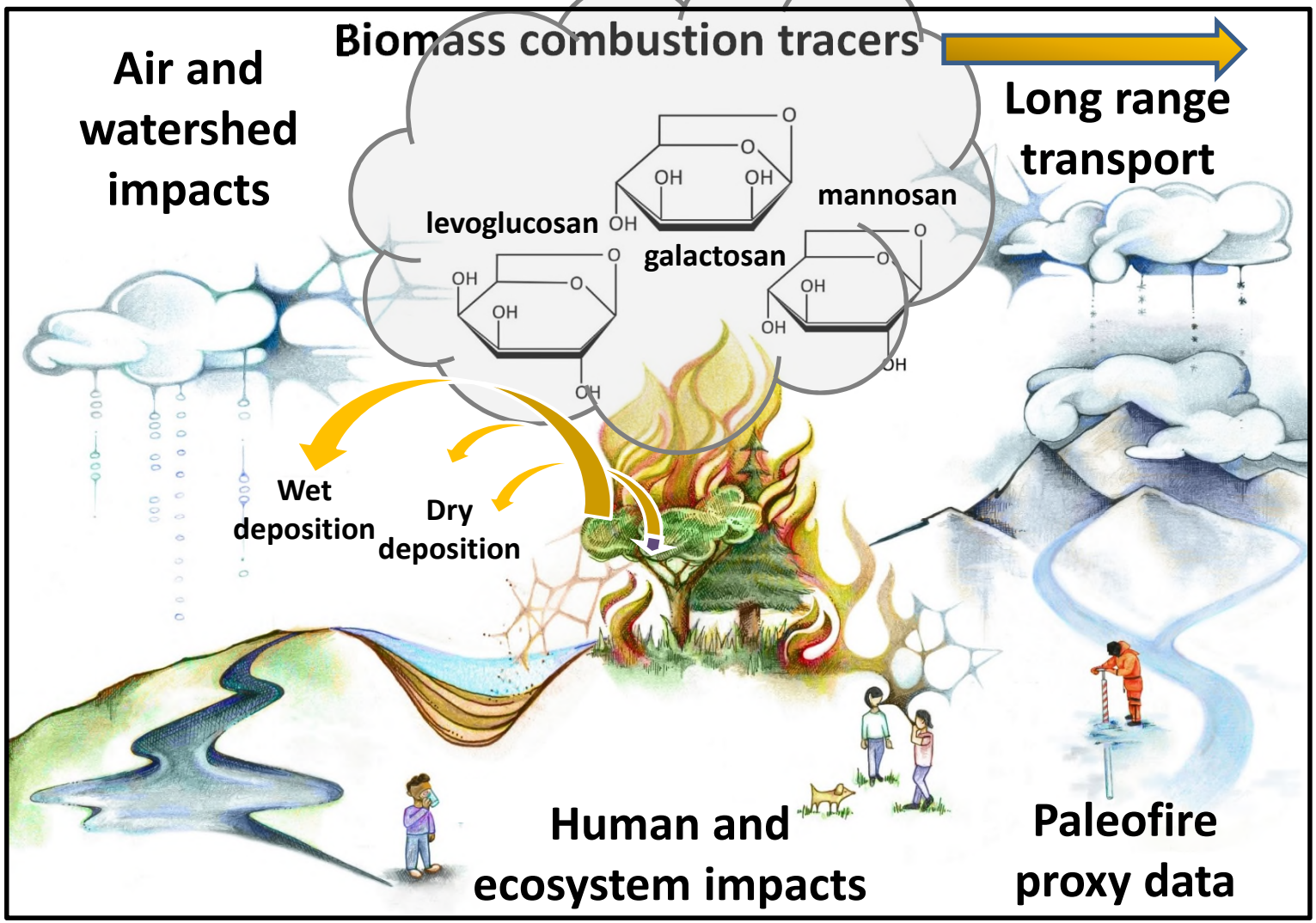
Natalie Kehrwald, Phd USGS

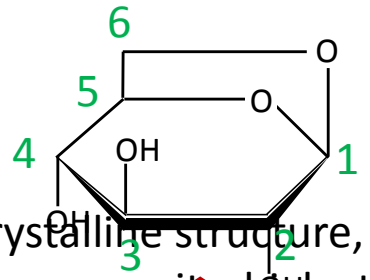
J. Jasmann, N. Kehrwald, L. Barber. (2019) Ultrasensitive, simultaneous determination of monosaccharide anhydride (MA) stereoisomers by gas chromatography - tandem mass spectrometry (GC/MS/MS). (in review). Graphic prepared by Mary S. Brink.



Wildland fires – interconnected with climate change, droughts, global carbon cycle, ecosystems, air quality, water quality, and infrastructure

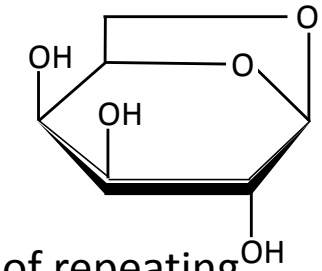
levoglucosan

(1,6-anhydro-β-D-glucopyranose)



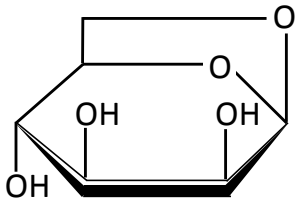
galactosan

(1,6-anhydro-β-D-galactopyranose)



mannosan

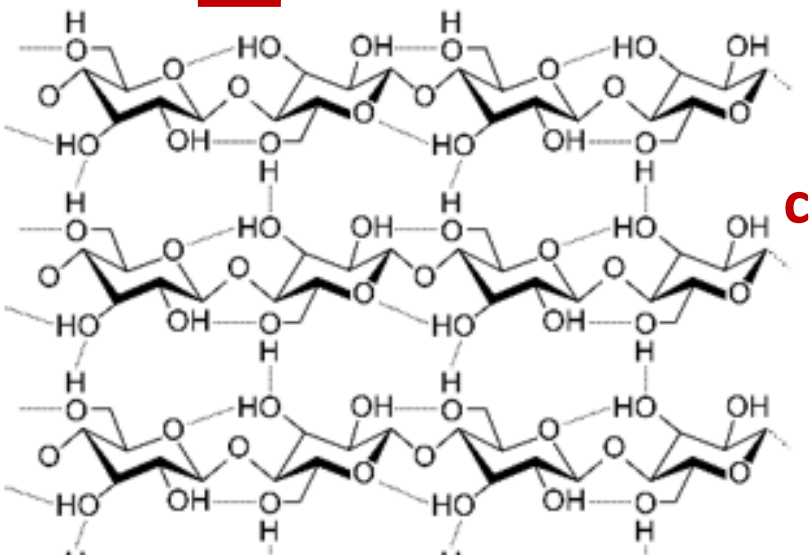
(1,6-anhydro-β-D-mannopyranose)



crystalline structure, many 1000s of repeating glucose units, high structural strength

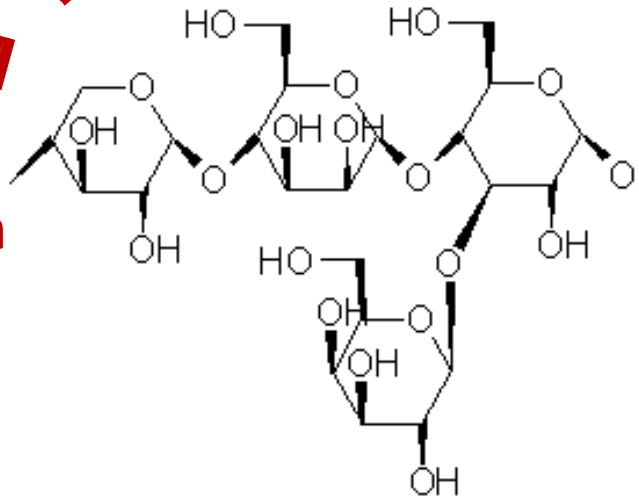
stable
semi-volatile
soluble

matrix polysaccharide, variety of different simple sugars, low structural strength



Cellulose

biomass combustion reaction



- Xylose - ß(1,4) - Mannose - ß(1,4) - Glucose -
- alpha(1,3) - Galactose

Hemicellulose

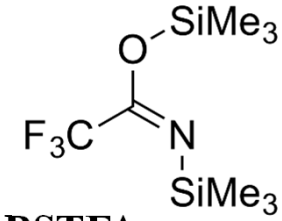
Both images sourced from commons.Wikipedia.org

Monosaccharide anhydrides are fingerprints of biomass fire activity

Ranging from ancient fire emissions to modern air and water quality

Spike ^{13}C-Levoglucosan isotopic internal standard

Collect 1.0 ml of melted ice core segment into reaction vial



BSTFA
N,O-*bis*(trimethylsilyl) trifluoroacetamide

Oven evaporation to dryness

Derivatization 60°C 3 h
200 µl BSTFA + 10% TMCS : pyridine (2:1)

Gas Chromatography
DB-5MS UI column of typical 30 m length

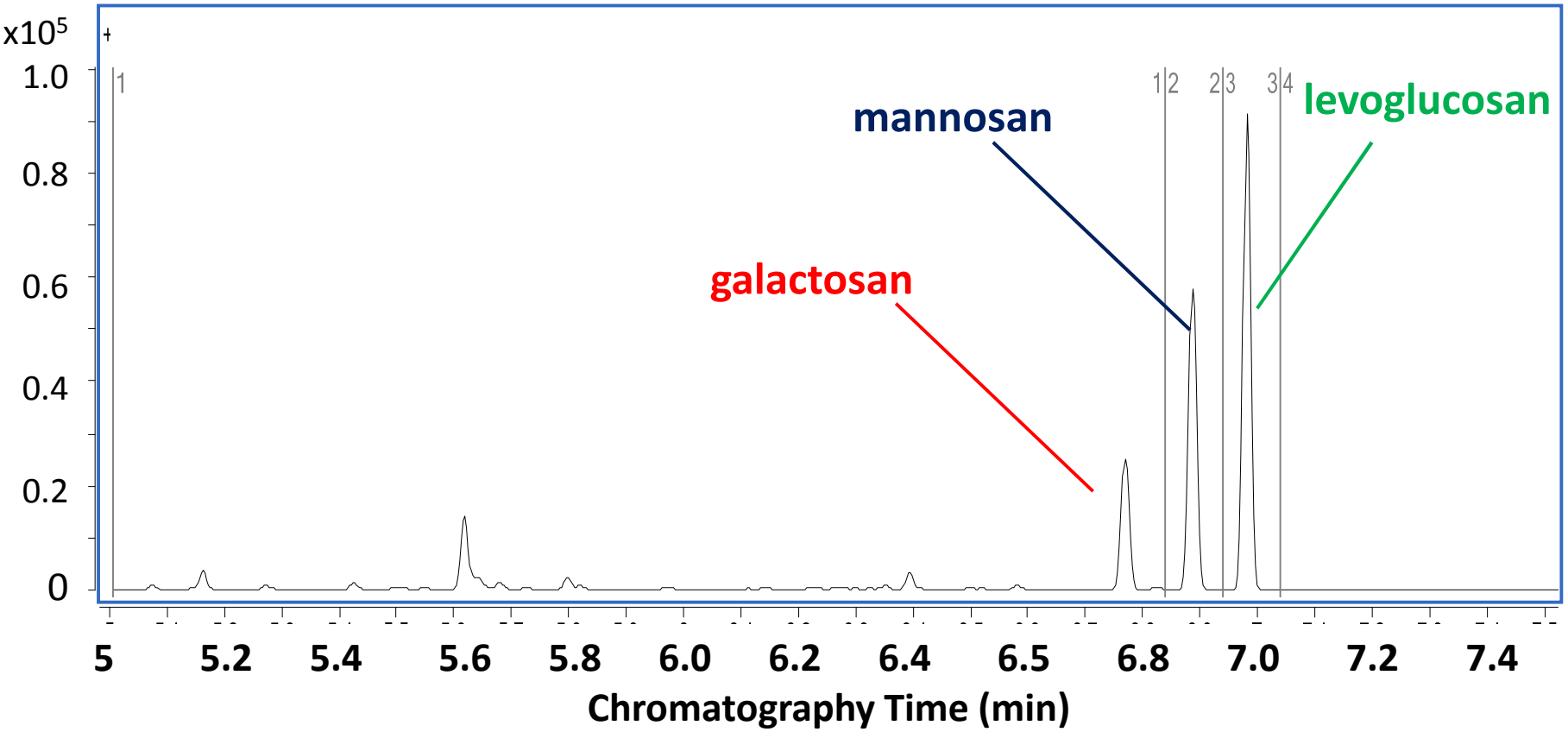
m/z 333>103
m/z 333>171
m/z 333>143

Tandem Mass Spectrometry MRM
Detection Limit at 70 to 200 ppt

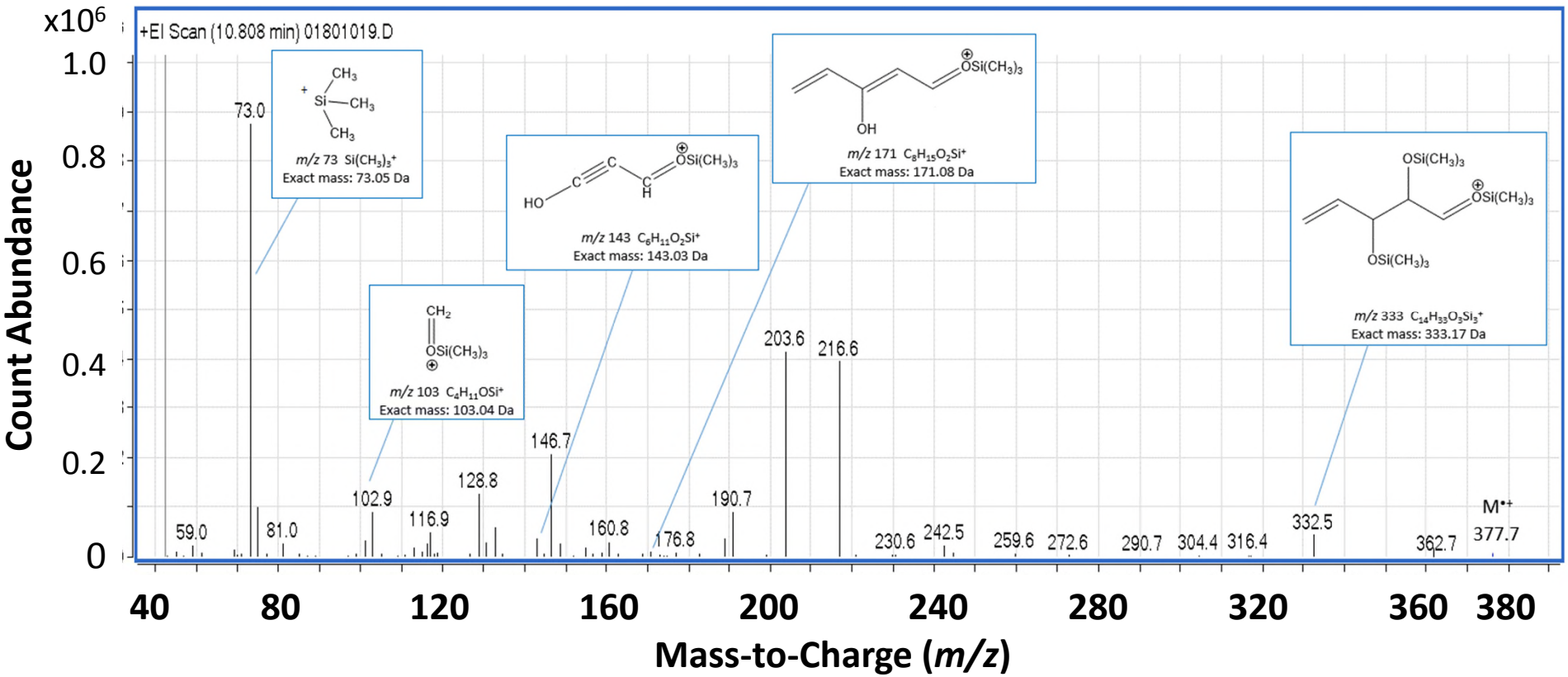
USGS
science for a changing world

Baseline chromatographic resolution achieved by GC-MS/MS

Gas Chromatogram for trimethylsilyl-derivatized Alaskan ice core sample

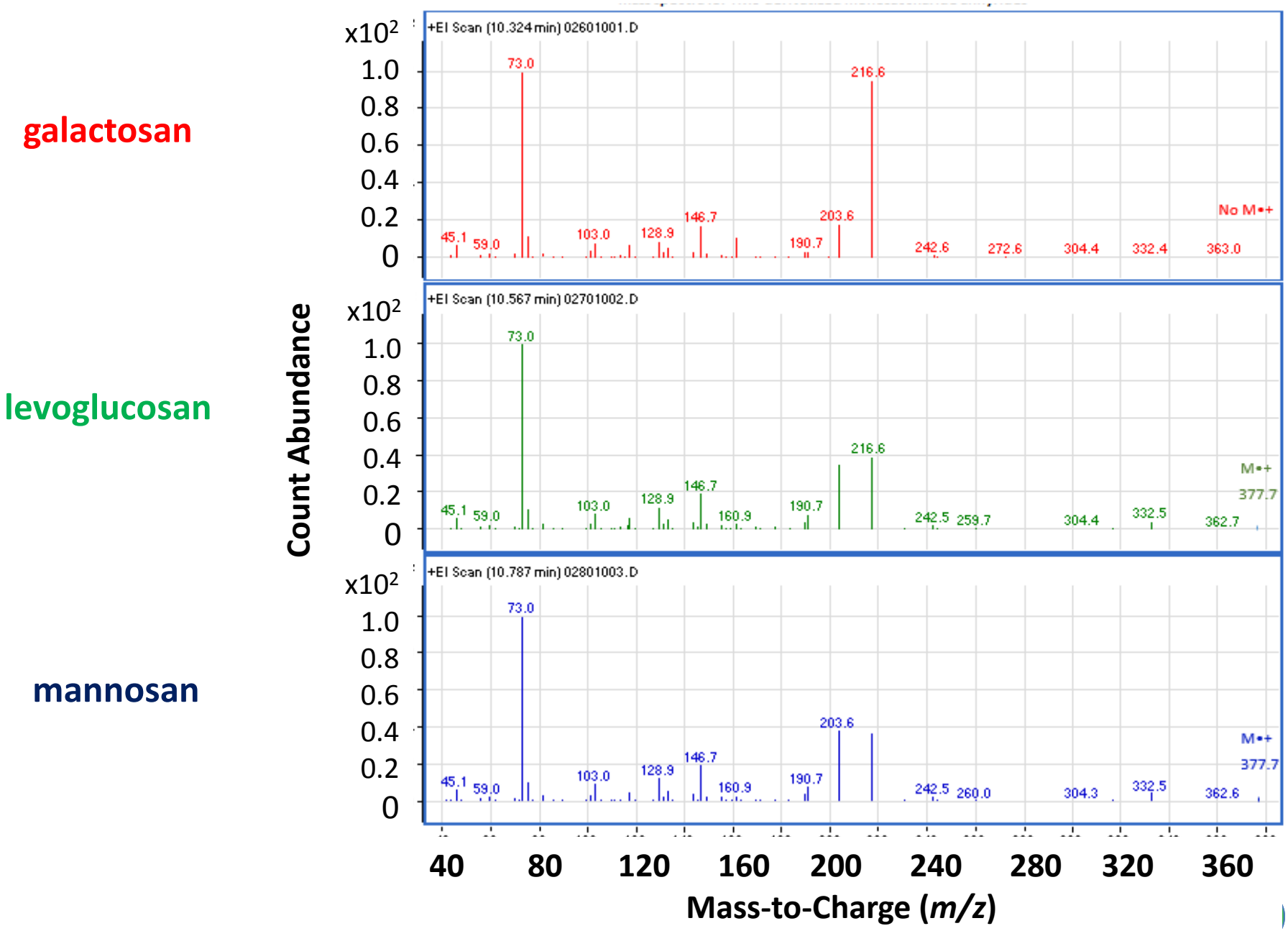


Mass Spectrum (full scan) for trimethylsilyl-derivatized levoglucosan

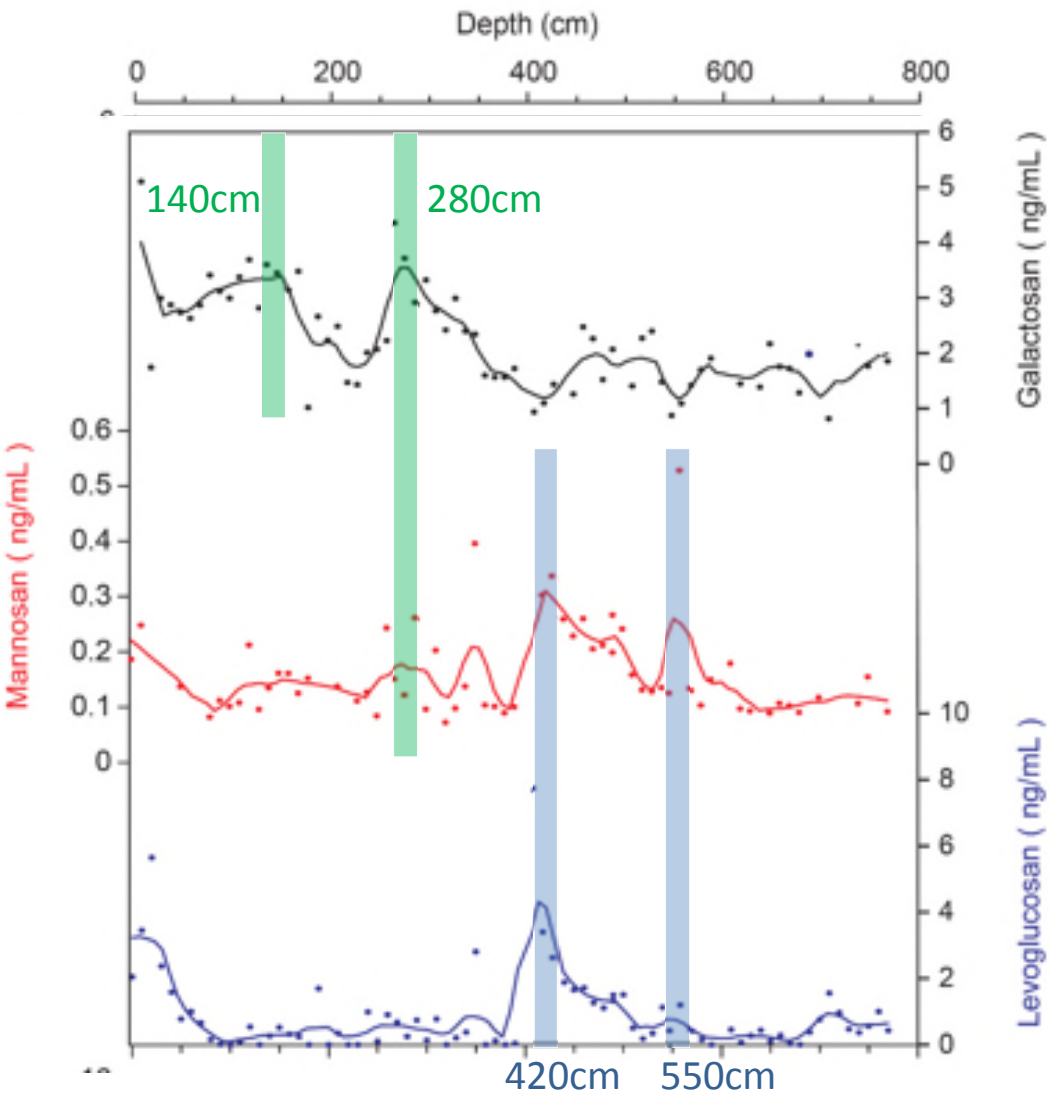


- **Ultra sensitivity with small volume samples**
- **High certainty of analyte identification and quantification**
- **Fast method with little minimal preparation**

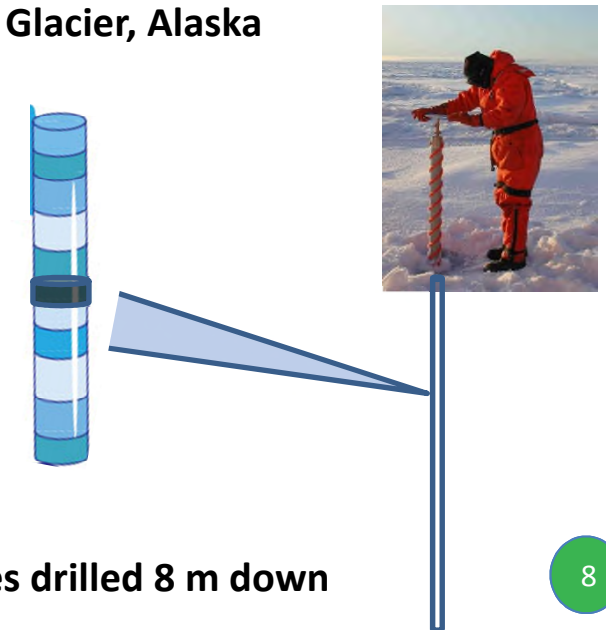
Mass Spectra (full scan) for trimethylsilyl-derivatized MA stereoisomers



Juneau Icefield Data, Alaska Core 3 depth to 8 m (decades old)

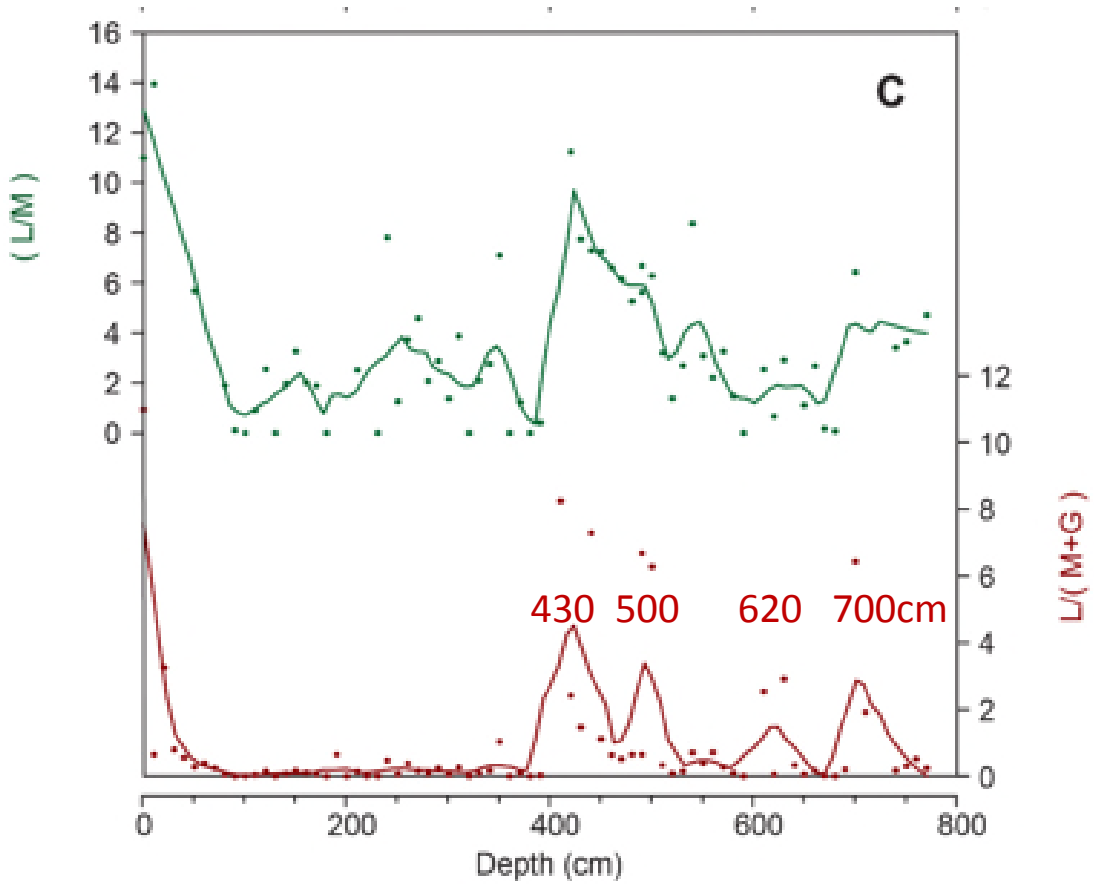


Juneau Icefield Research Program
Llewelly Glacier, Alaska



Ice cores drilled 8 m down

Ratios of monosachharide anhydrides can help characterize types of biomass burning

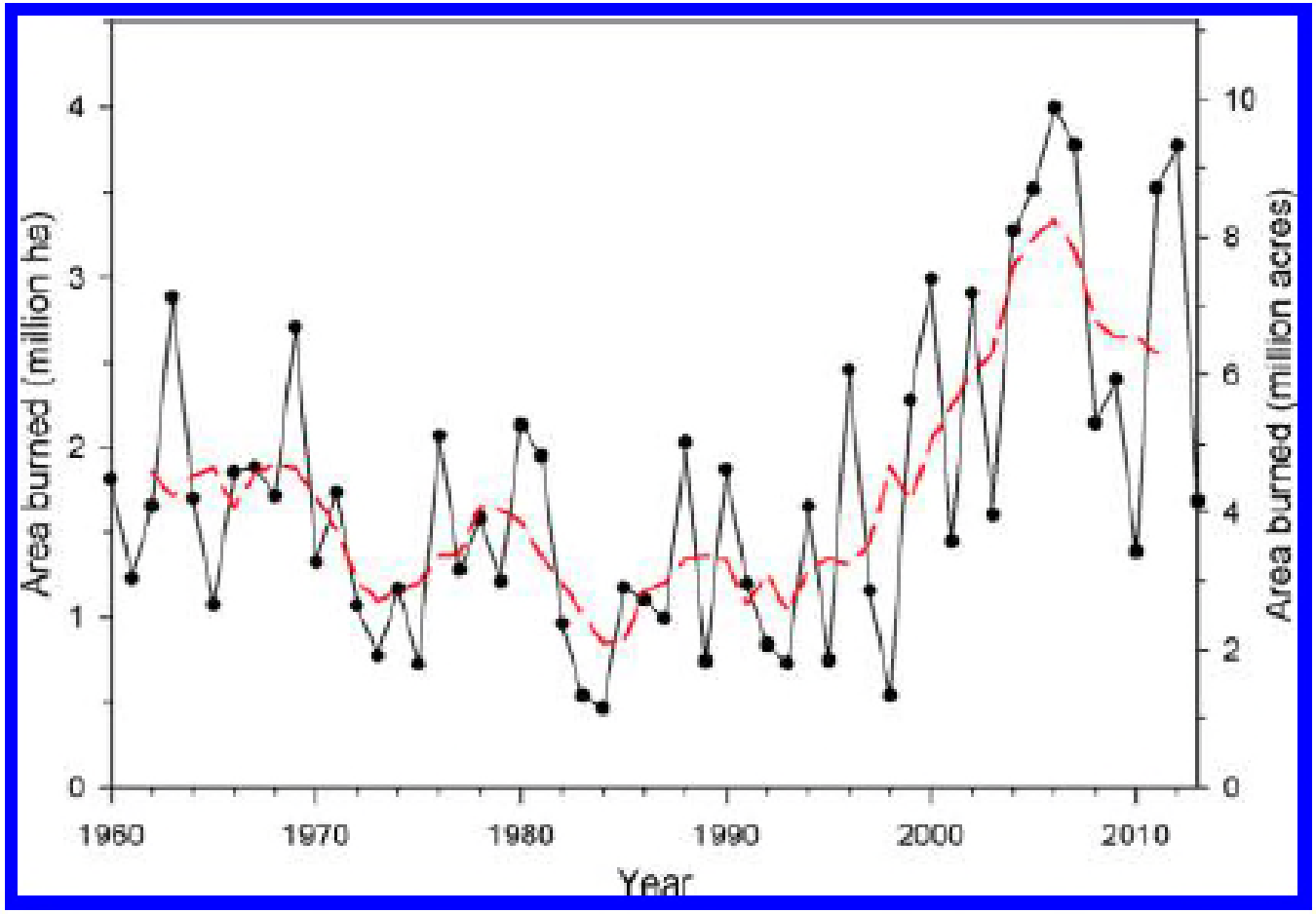


L/(M+G) ratio is characteristic of grassland burns

rather than burning of forested areas

Wildland Fires are occurring with increasing frequency and intensity

In North America and Australia, mega-fires now account for approximately 90–95% of the annual area burned, even though they represent <1% of the number of wildfires.



National Interagency Fire Centre. Total wildland fires and acres (1960–2013). http://www.nifc.gov/index.html

Wildfire Impacts on Water Quality

Photo credit: Kent Porter/Santa Rosa Press Democrat
A worker takes samples of water after carcinogenic benzene was unexpected detected in Santa Rosa's water system after 15,000 hectares of Sonoma wine country burned in Fall of 2017. Wilson, E.K. C&EN Volume 96, Issue 26.

Photo credit: Jackson Webster
The waters of Butte Creek, which drains from the burned town of Paradise, CA, are dark brown and smell of smoke. Bourzac, K. C&EN Volume 96, Issue 48.

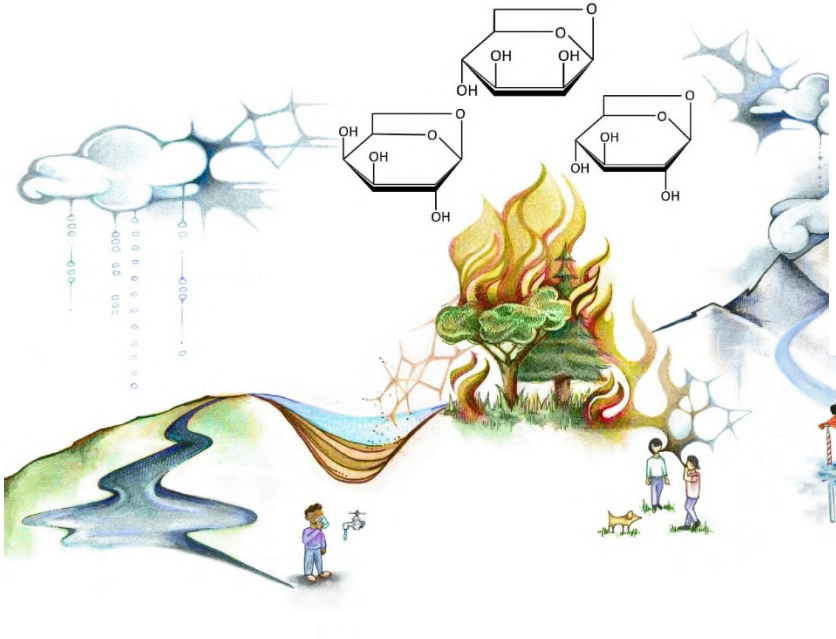
- A better understanding is needed of the effects of wildfire on water quality in immediate watershed and in those watershed where wet deposition can occur with smoke constituents
- To inform adaptation and mitigation strategies to protect globally critical water supplies originating in forested environments.

Wildfire Impacts on Water Quality

Examples of unburned (left) and postfire (right) stream beds.
Source: Southern Rockies Watershed Project
U. Silins, et al. Ecohydrology, 2014, DOI: 10.1002/eco.1474.

Other Research Questions this method could help to address

- How does our recent increase in fire activity compare to historic fire records stored in the glaciers and icefields?
- Are fossil fuel combustion activities (e.g. coal-burning powerplants) bigger contributor to mercury deposition in water sheds than biomass combustion activites (wildland fires)?



- Are cars and cows bigger contributors of nitrogen deposition in sensitive natural areas like Rocky Mountain National Park than biomass combustion (wildfires, agriculture burns, fireplaces)? Use National Atmospheric Deposition Program's network of wet deposition collections.

Could levoglucosan in surface water samples be used as early warning signal for more toxic combustion products like polycyclic aromatic hydrocarbons (PAHs)?