

Organic Aerosol Fractionation Using Subcritical Water

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What is subcritical water?

- Subcritical water can be defined as hot water under sufficient pressure to maintain the liquid state. (hot water, superheated water)

Why subcritical water?

- The polarity can be controlled with change of temperature.
- As the polarity of water is controlled, solubility is controlled. The solubility of PAHs and pesticides increases by an order of magnitude with every 50 °C.
- Water is not toxic.



Properties of Subcritical Water

	25°C	300°C
dielectric constant (ϵ)	80	20
polarity	high	low
similar organic solvents	none	methanol, acetonitrile
compounds extracted	high polarity (e.g. strong organic acids)	low polarity (e.g. PCBs, PAHs)



Characterization of Organic Aerosols

Limitation of current methods

- Organic solvents employed extract non-polar or slightly polar organic compounds (20-50% of carbonaceous extracted).
- GC/MS analyses (not suitable for all compounds)

Our Approach

- Sequential fractionation with subcritical water
- Characterization using toxicity tests

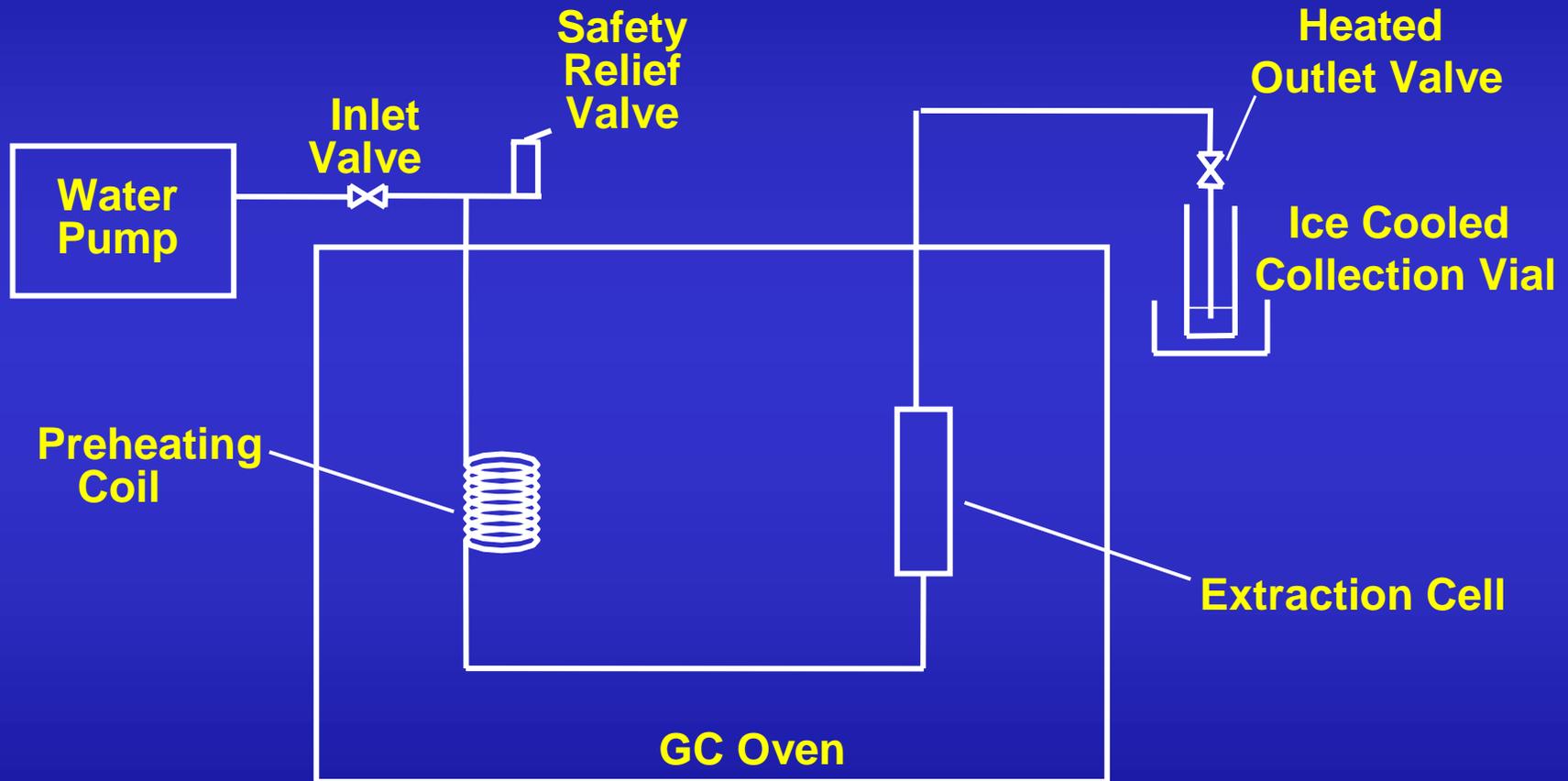


Fractionations with subcritical water were performed with two common carbonaceous aerosols:

- **Wood smoke particulate (polar matrix)**
- **Diesel exhaust particulate (relatively nonpolar matrix)**



Subcritical Water Extraction Apparatus



Toxicity tests

BACTERIAL

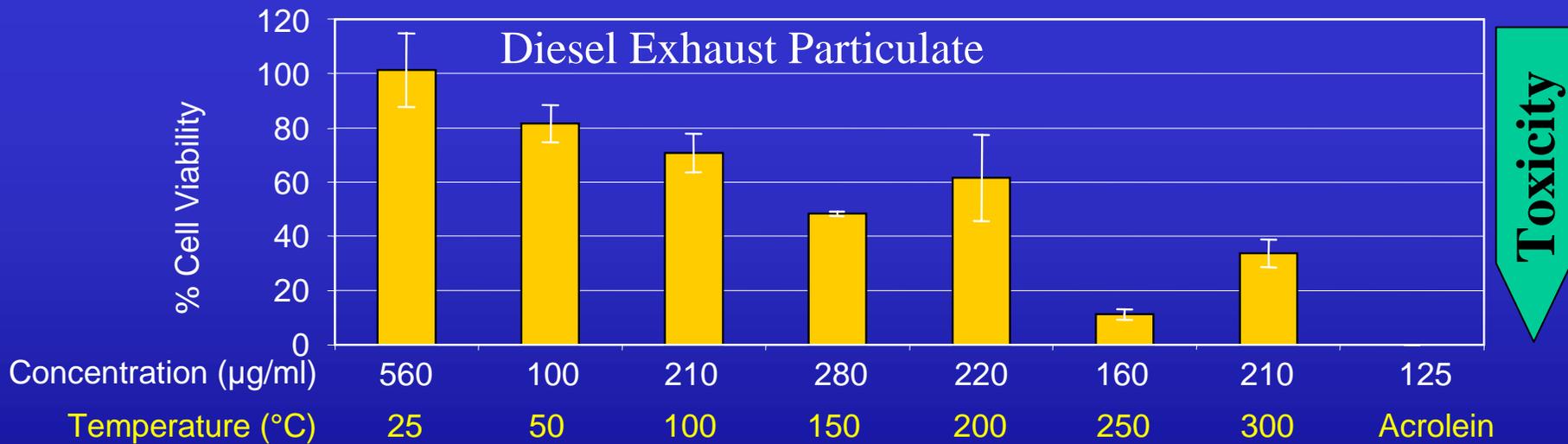
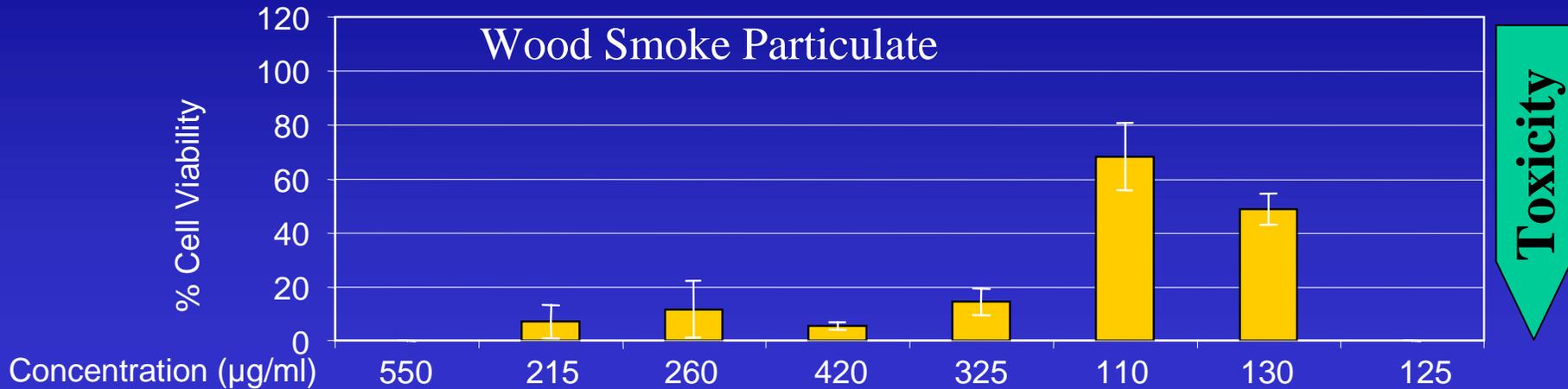
- **Polytox:** Rapid test for measuring the toxicity of wastewater based on the inhibitory effect on respiration rate of mixed bacterial cultures.
- **SOS chromotest:** Genotoxicity test based on DNA damage.

MAMMALIAN

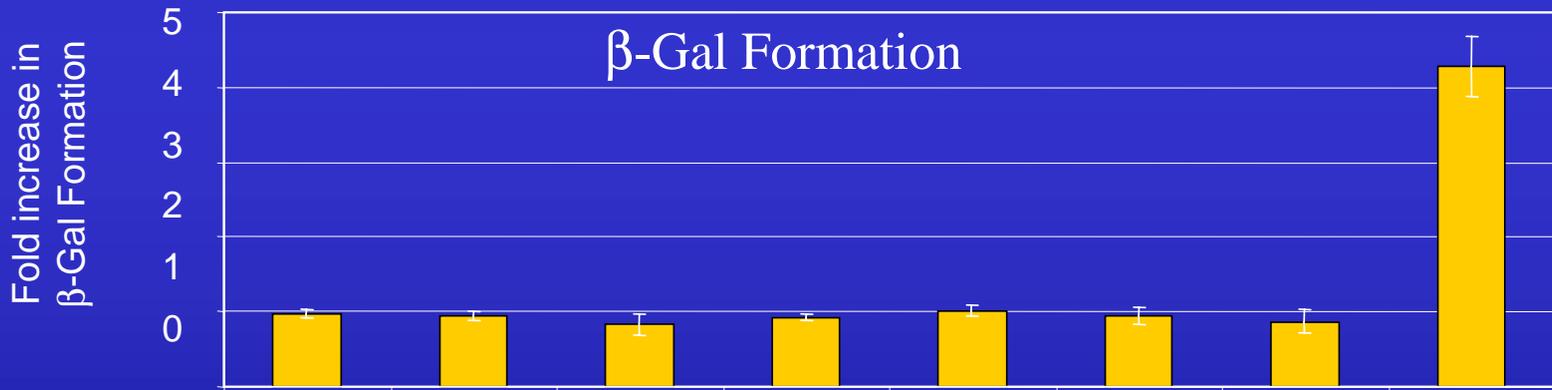
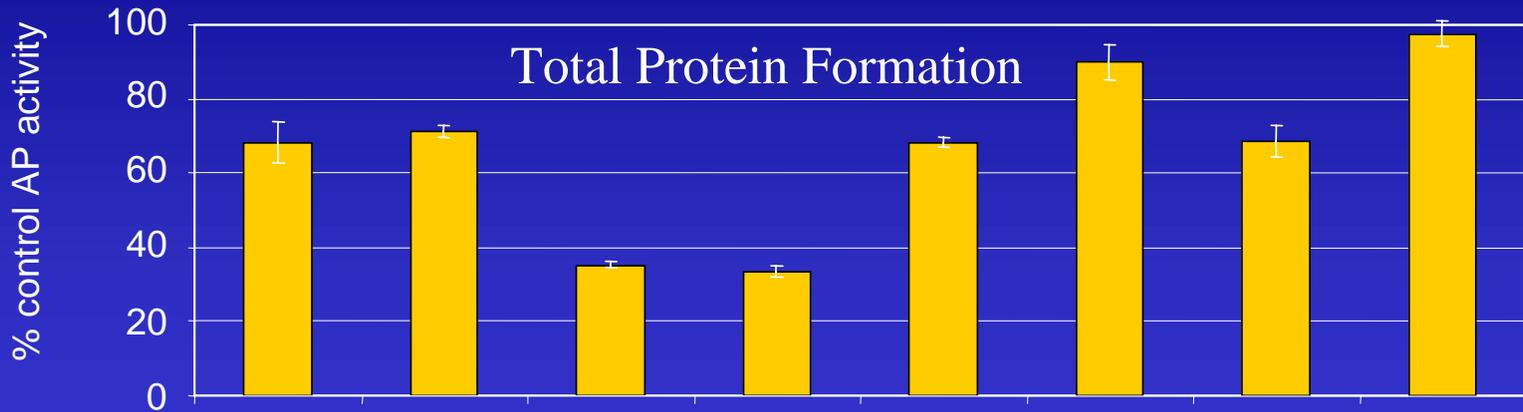
- **Cytotoxicity test:** Based on the inhibited mammalian cells (COS) viability.
- **Mitochondrial respiration**



Cytotoxicity – Viability of Mammalian Cells



SOS Chromotest - Wood Smoke Particulate

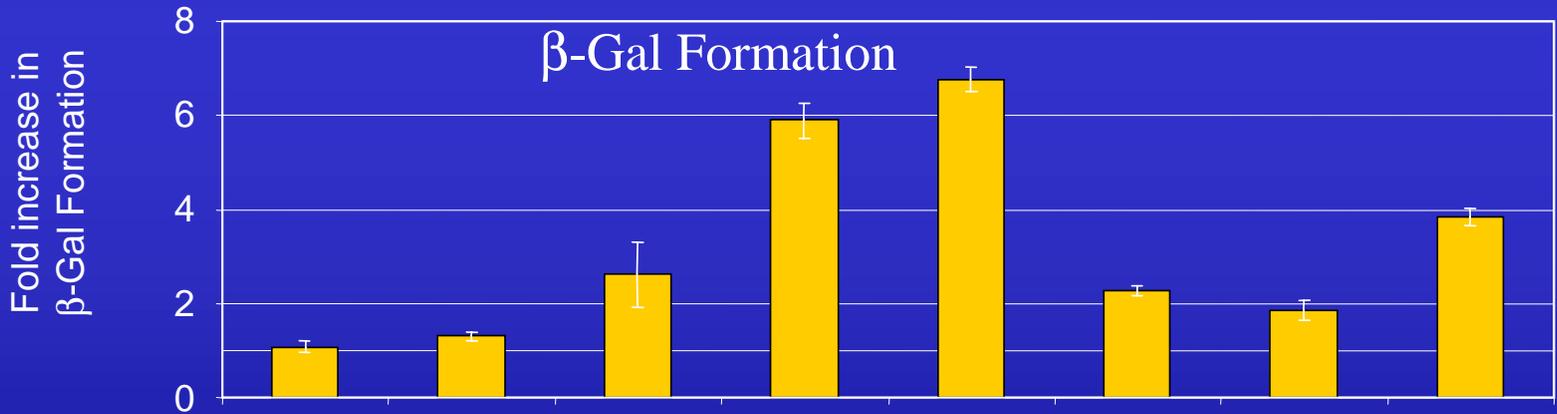
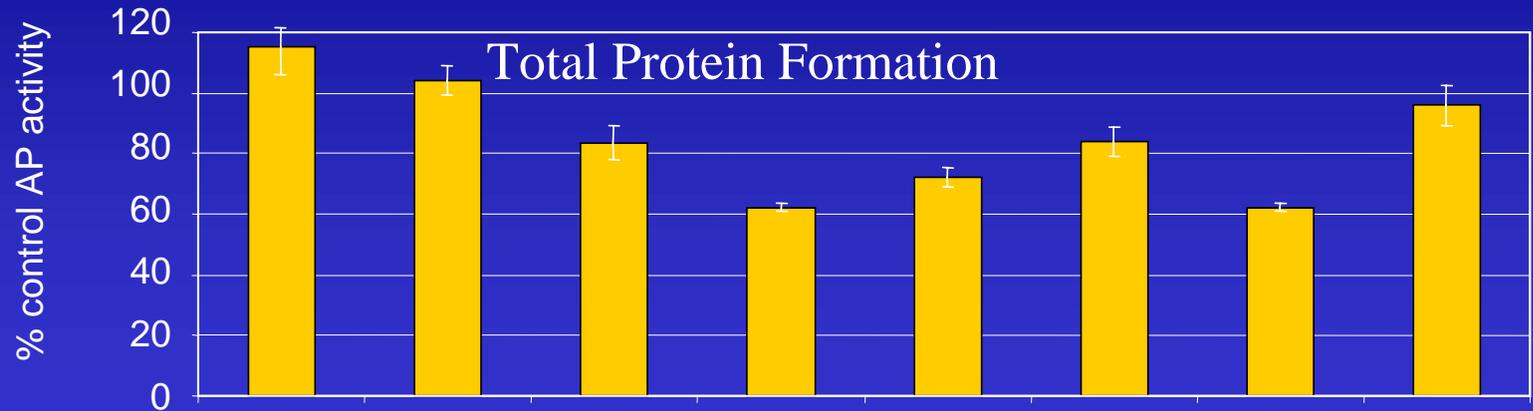


Concentration (µg/ml) 544 211 253 412 319 108 127 0.227
Temperature (°C) 25 50 100 150 200 250 300 NQO



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SOS Chromotest - Diesel Exhaust Particulate

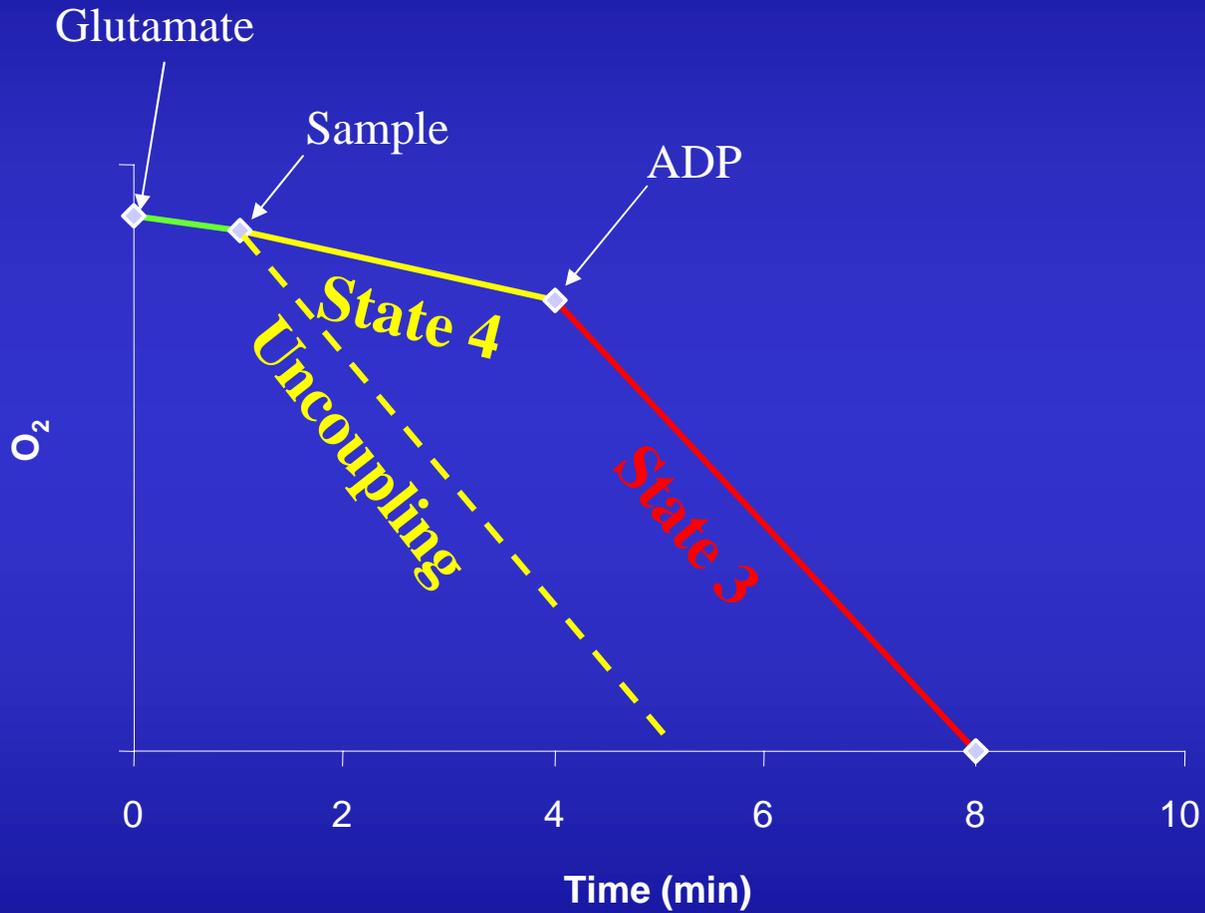


Concentration (µg/ml) 450 90 180 230 200 140 190 0.230
Temperature (°C) 25 50 100 150 200 250 300 NQO

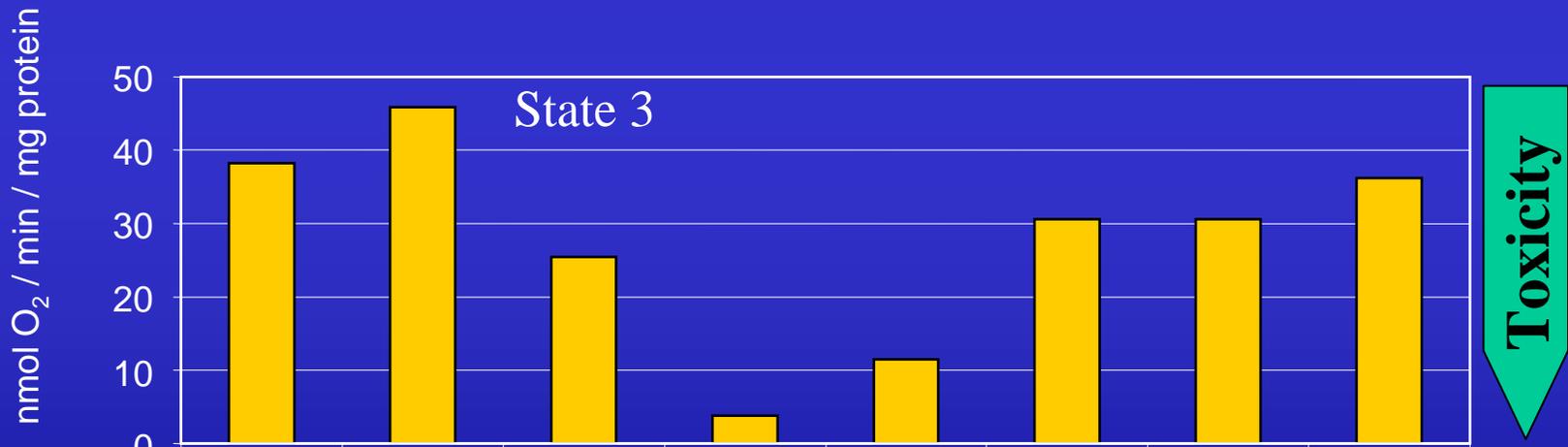
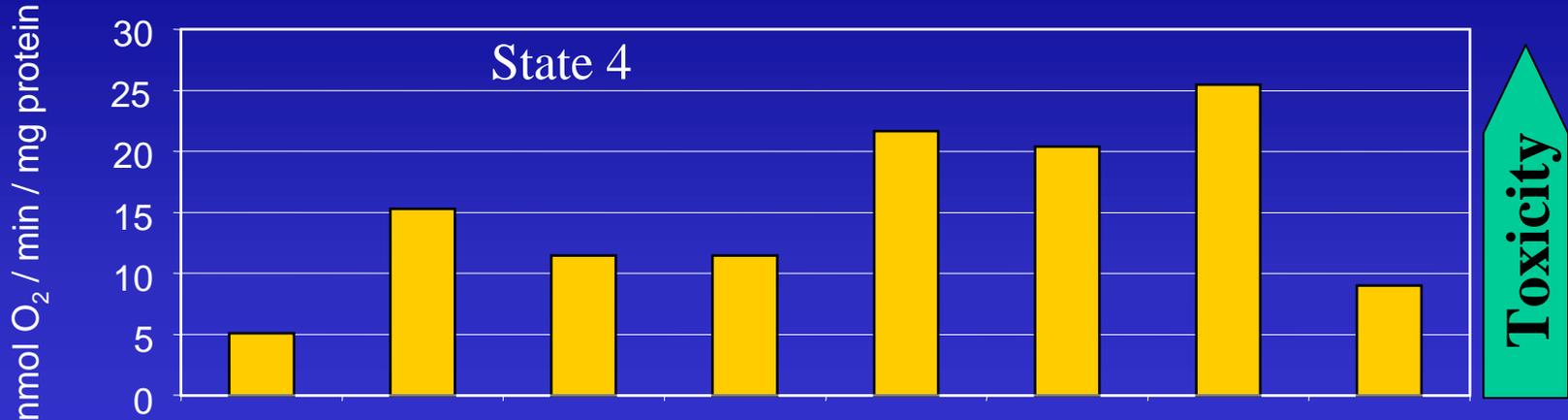


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Mitochondrial Respiration



Mitochondrial Respiration – Wood Smoke Particulate

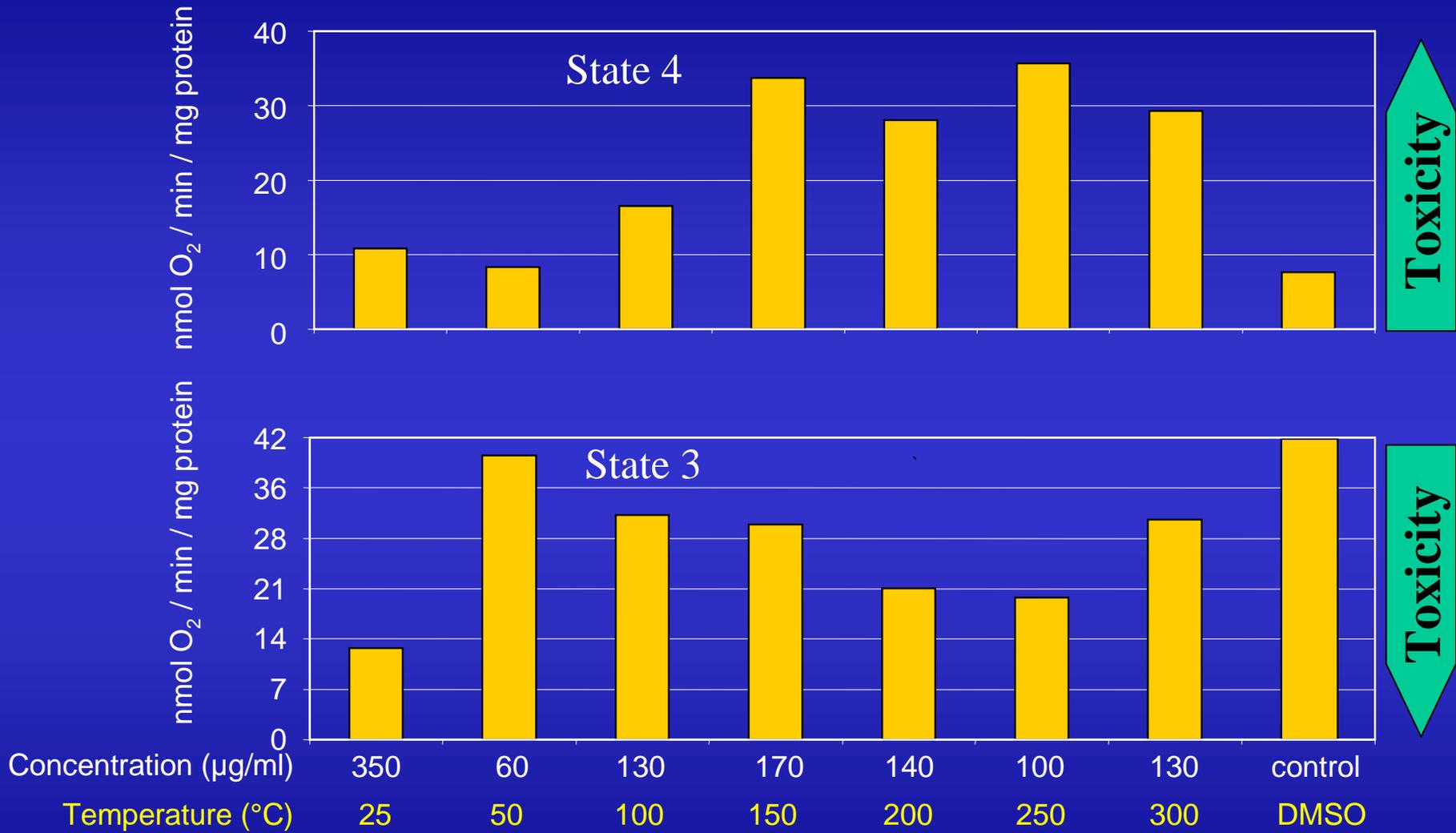


Concentration (µg/ml) 360 50 170 275 210 70 80 control
 Temperature (°C) 25 50 100 150 200 250 300 DMSO



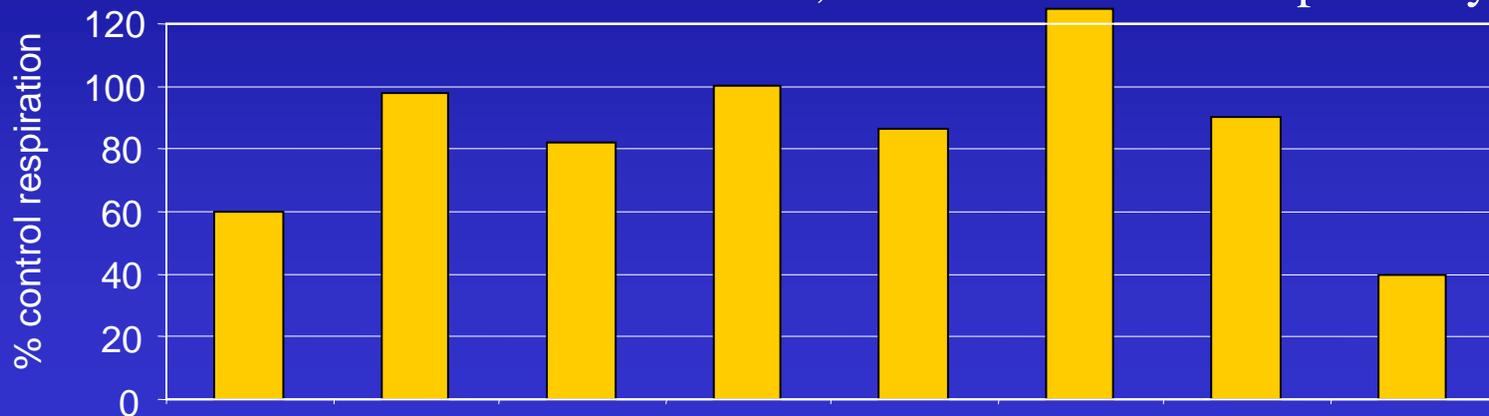
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Mitochondrial Respiration – Diesel Exhaust Particulate

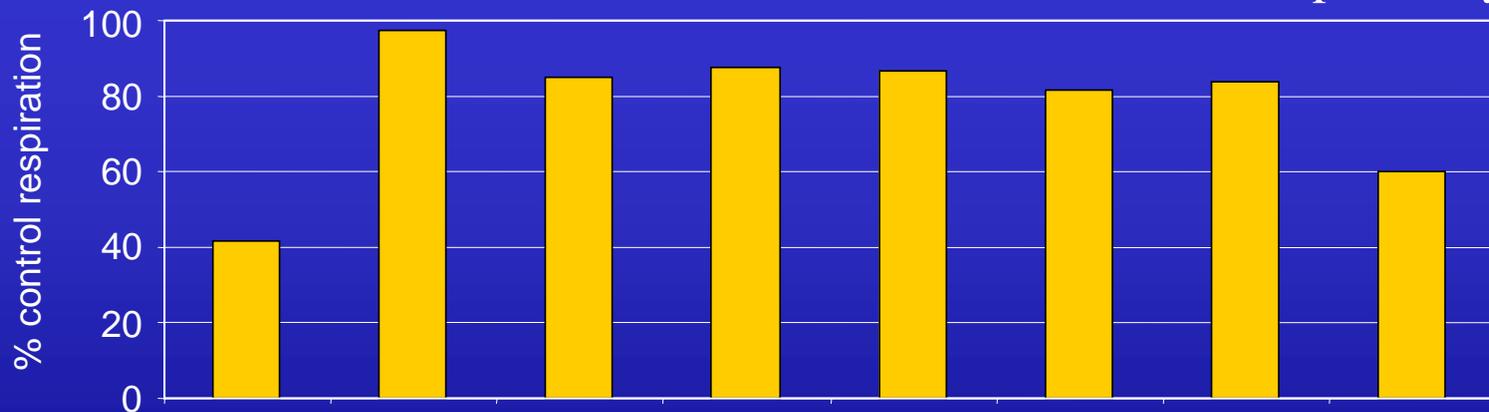


Bacterial Respiration (POLYTOX™) with Diesel Exhaust Particulate Water Extracts

Concentrated water extracts, 20% of each fraction per assay



Dried water extracts, dissolved in DMSO, 5% of each fraction per assay



Temperature (°C)

25

50

100

150

200

250

300

m-cresol

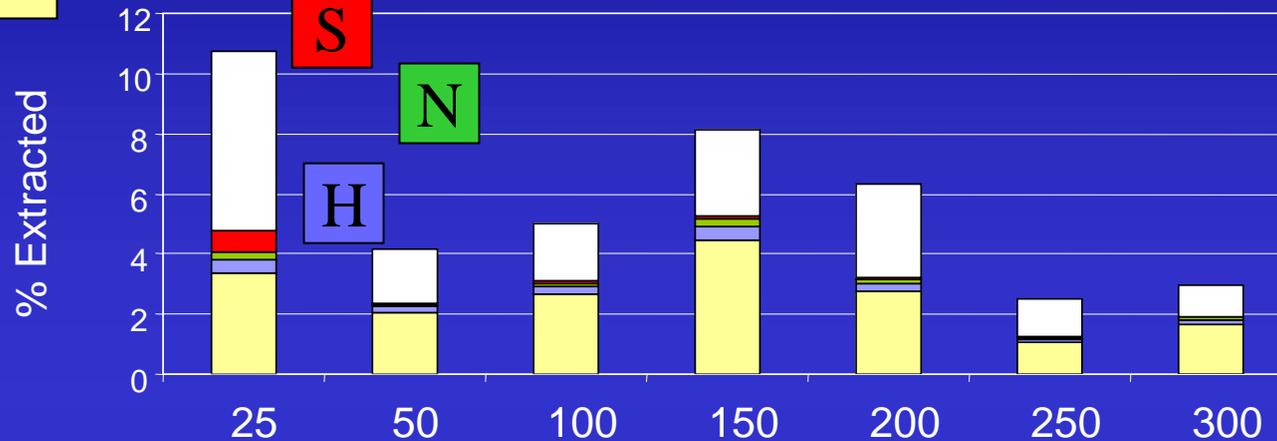


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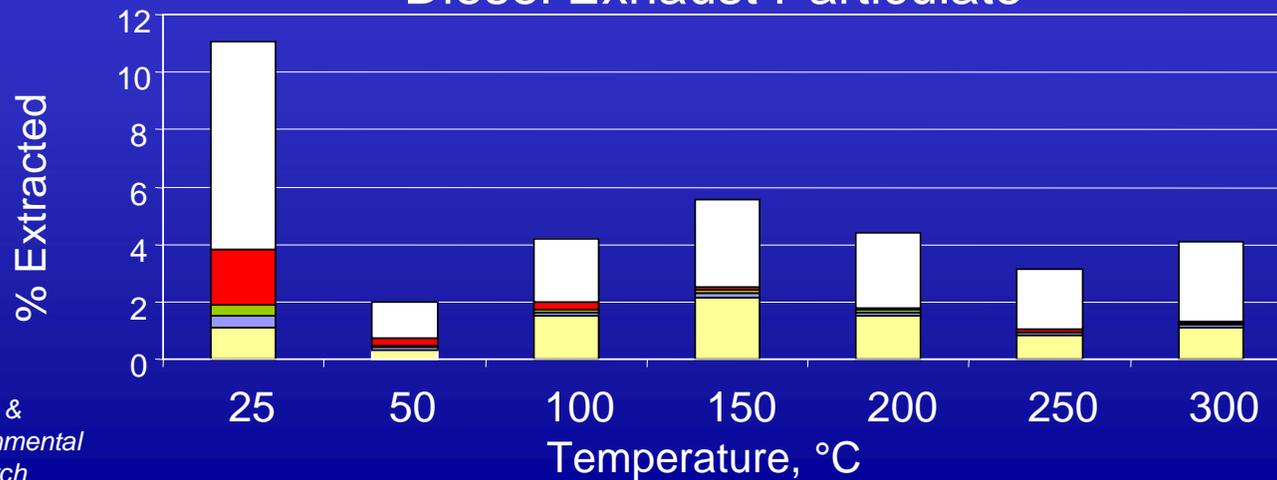
Fractionation of Aerosols with Subcritical Water

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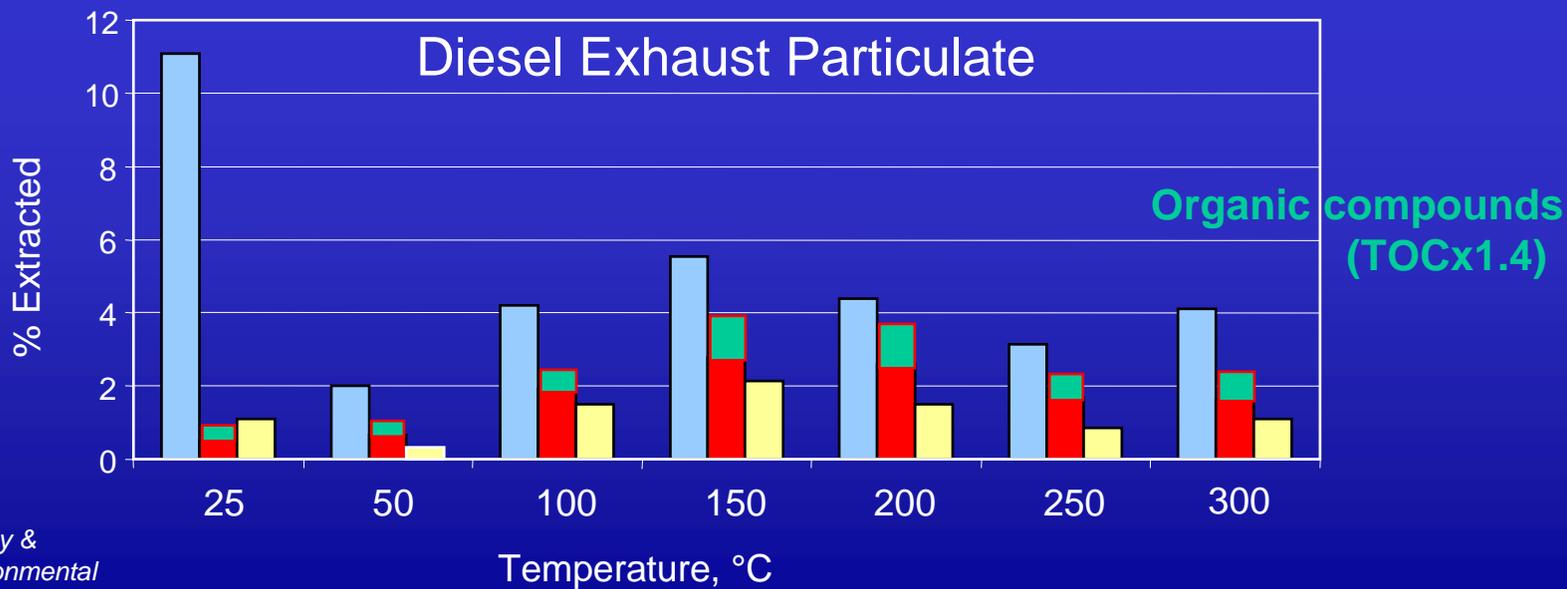
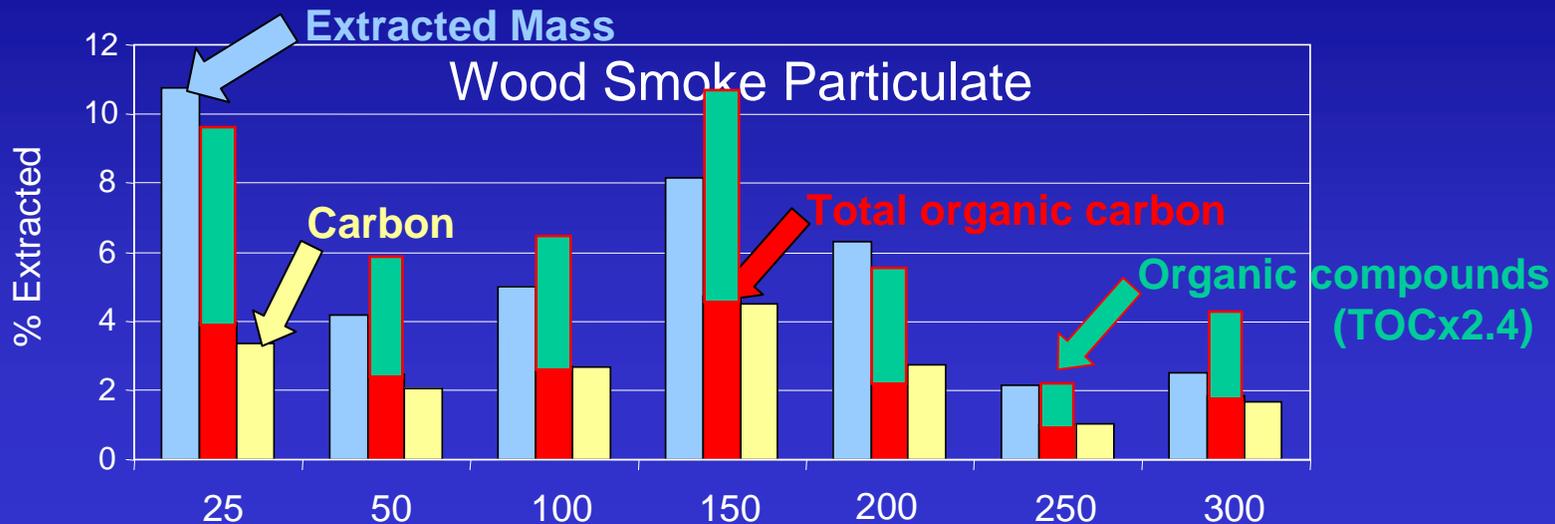
Wood Smoke Particulate



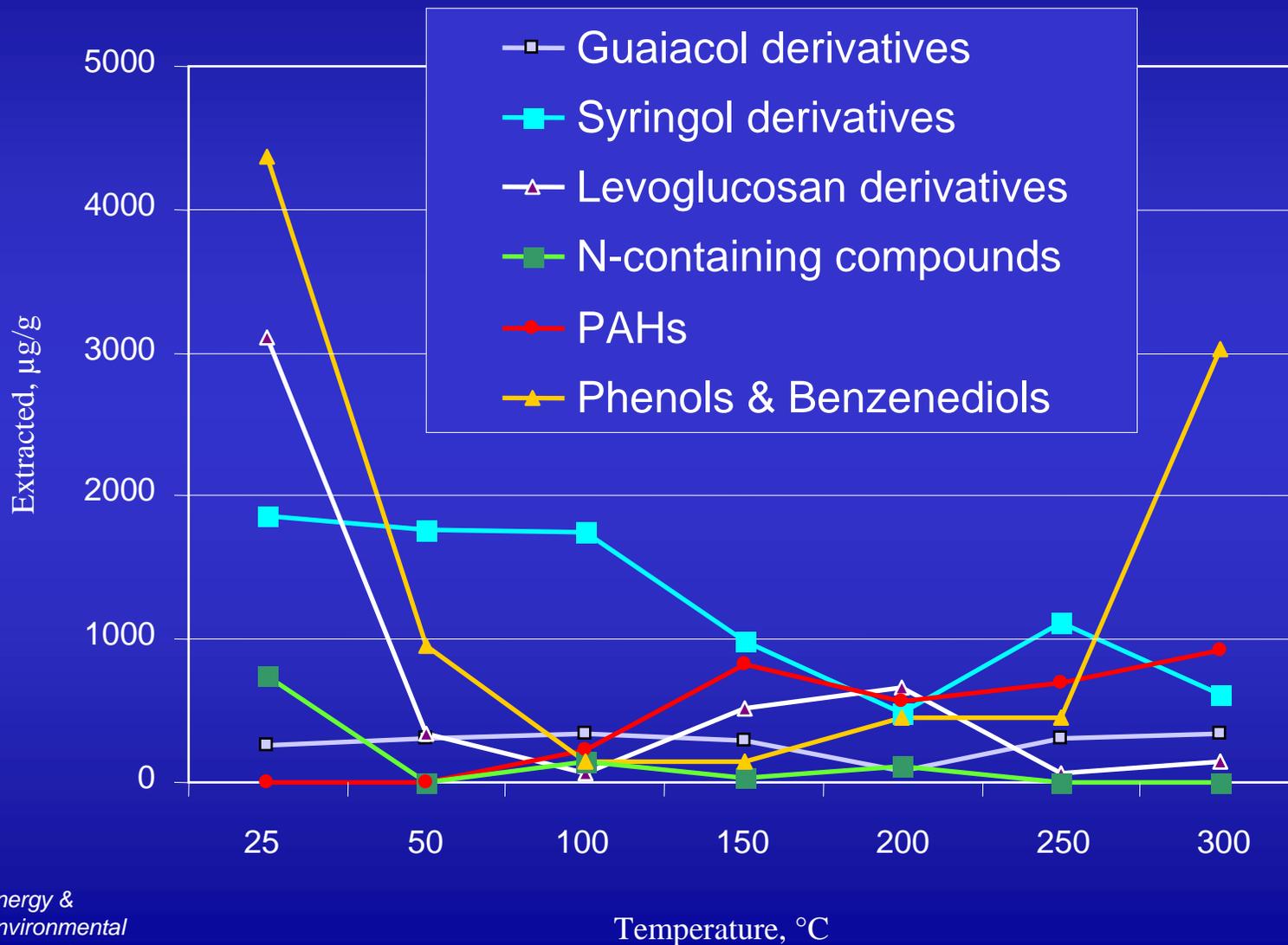
Diesel Exhaust Particulate



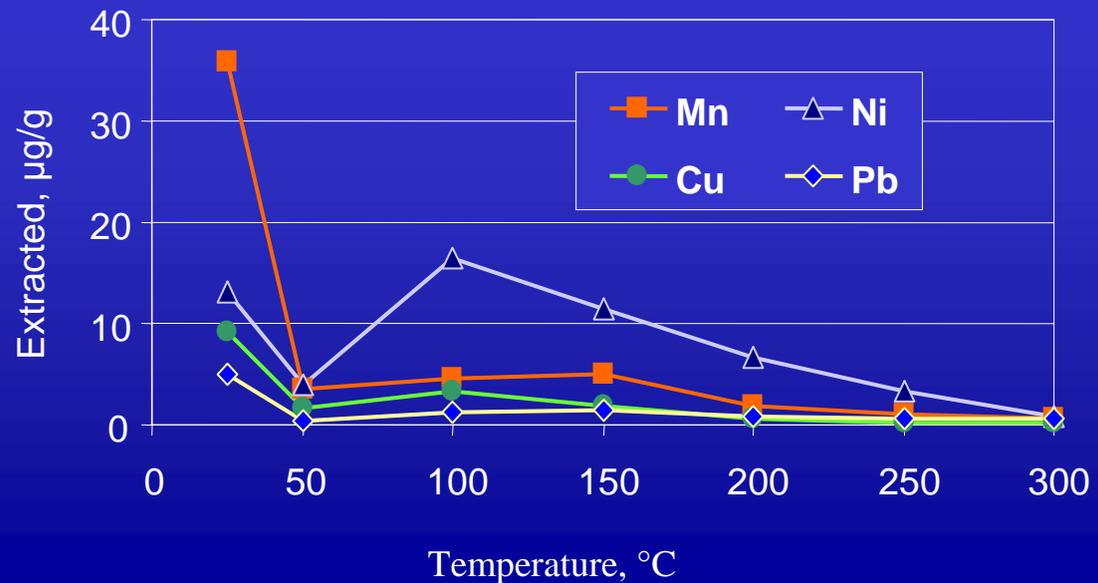
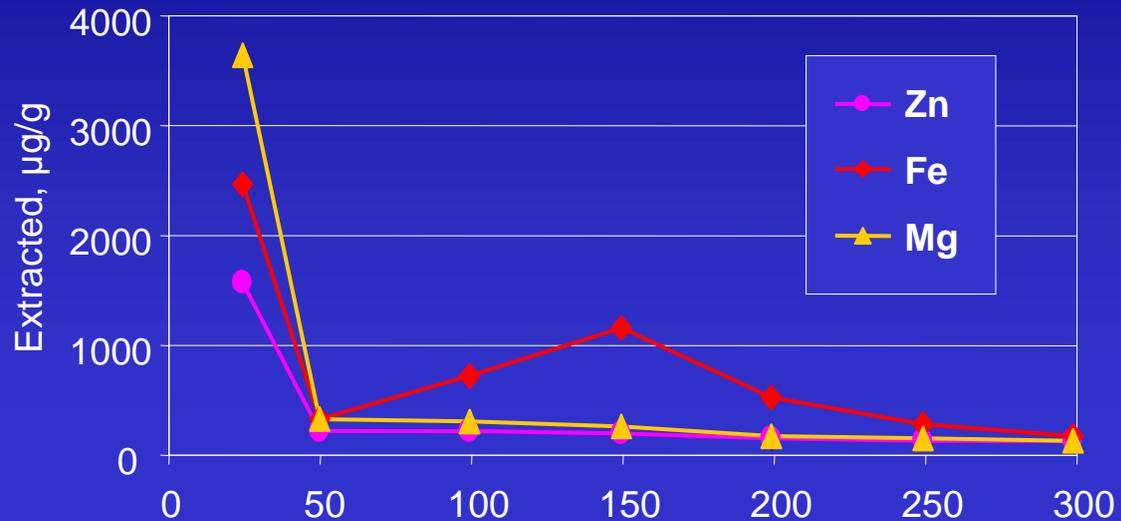
Determination of carbon and total organic carbon (TOC)



Distribution of Different Classes of Organics in Wood Smoke Particulate Extracts Collected at Different Temperatures



Metals Determined Using ICP/MS in Diesel Exhaust Particulate



Conclusions

- Subcritical water can selectively extract organics.
- High toxicity was found in the polar fractions, fractions which are not expected to be extracted by organic solvents. Except Polytox™ all test exhibited high sensitivity.
- GC/MS characterization of wood smoke particulate showed phenols, benzenediols and levoglucosan extracted preferentially in lower temperature fractions.
- Higher content of sulfur, magnesium, iron and zinc was found in the lower-temperature fraction of diesel exhaust.
- The results indicate that standard methods employing organic solvents neglect characterizing the polar fractions of aerosol particulate which are important from a toxicological point of view.

