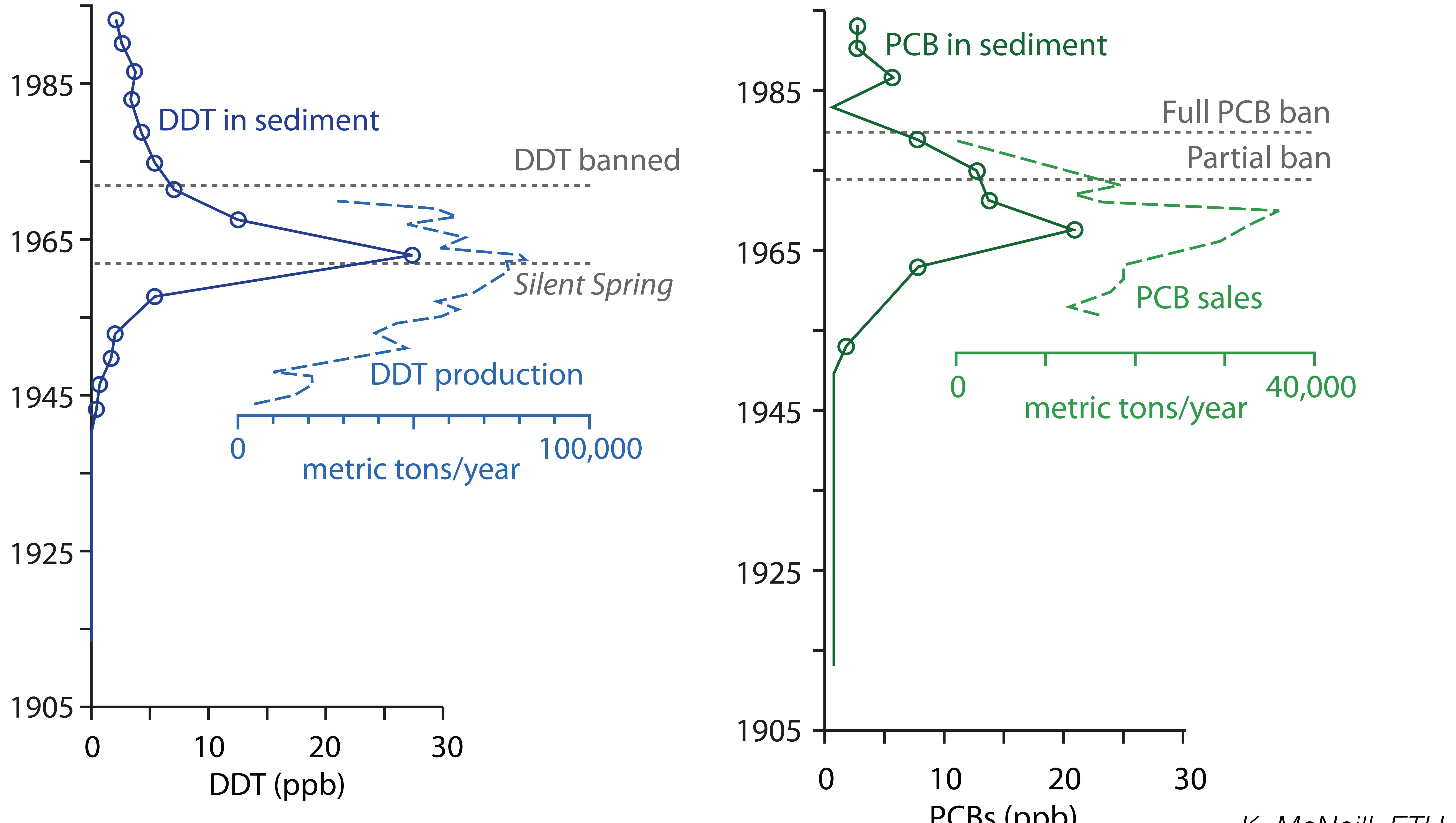
Simultaneous optimization of environmental and technical performance in materials and process design

Desiree Plata, PhD
Gilbert W. Winslow Career Development Assistant Professor
Civil and Environmental Engineering
Massachusetts Institute of Technology

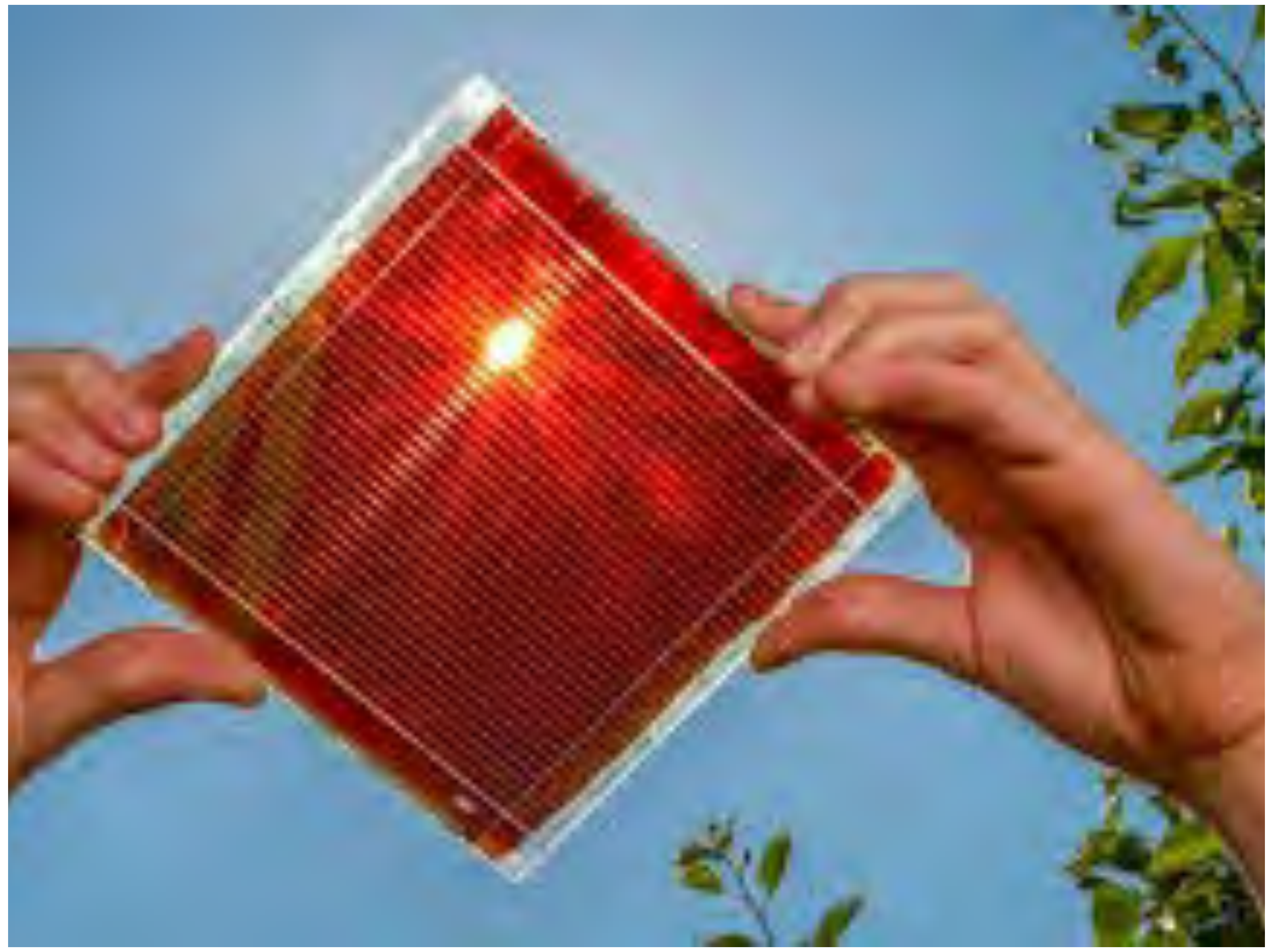
November 13, 2019
2019 MIT Research and Development Conference
Human and Technology Collaboration

Few chemicals are produced, used, and disposed of without release to the environment

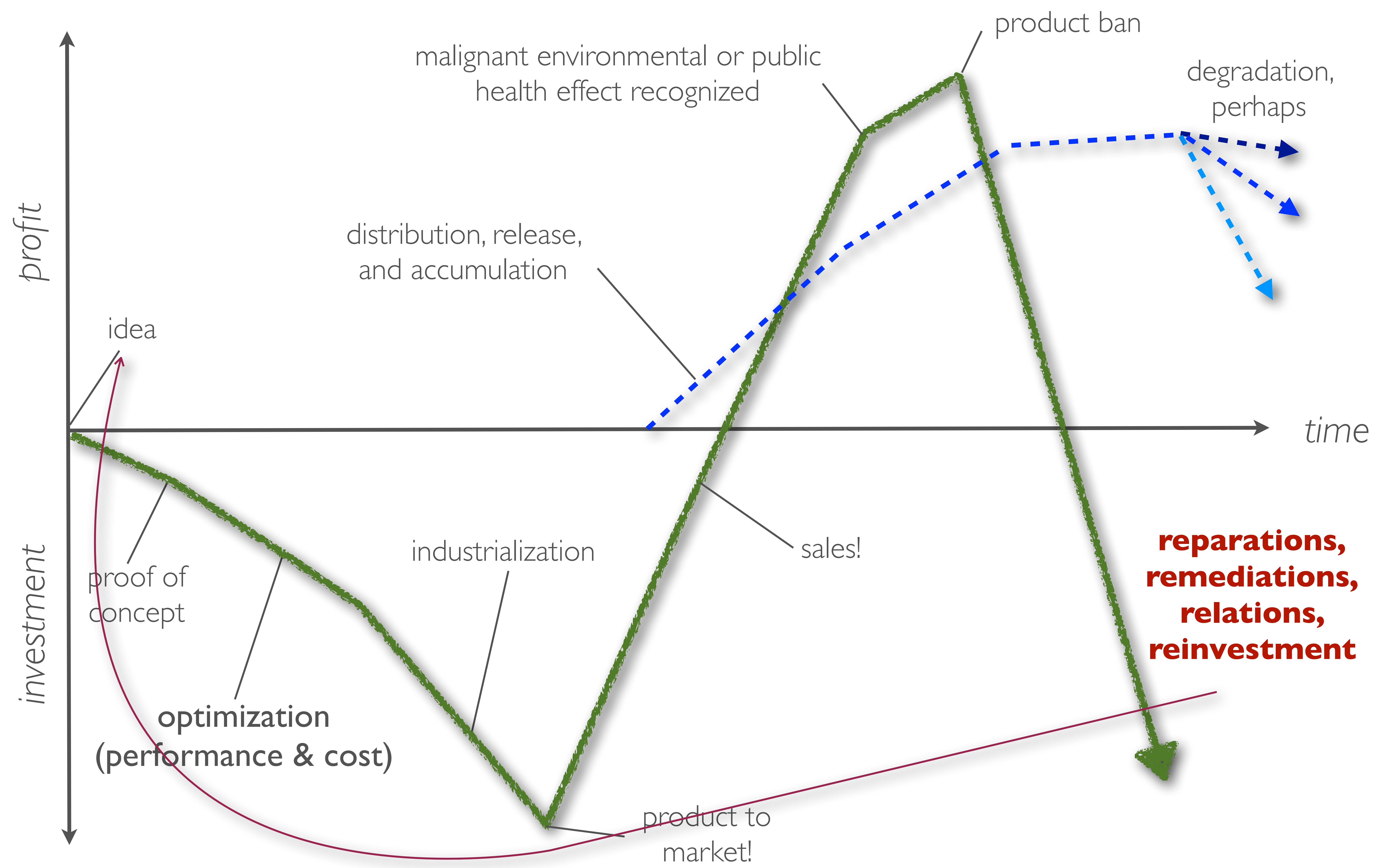


K. McNeill, ETH

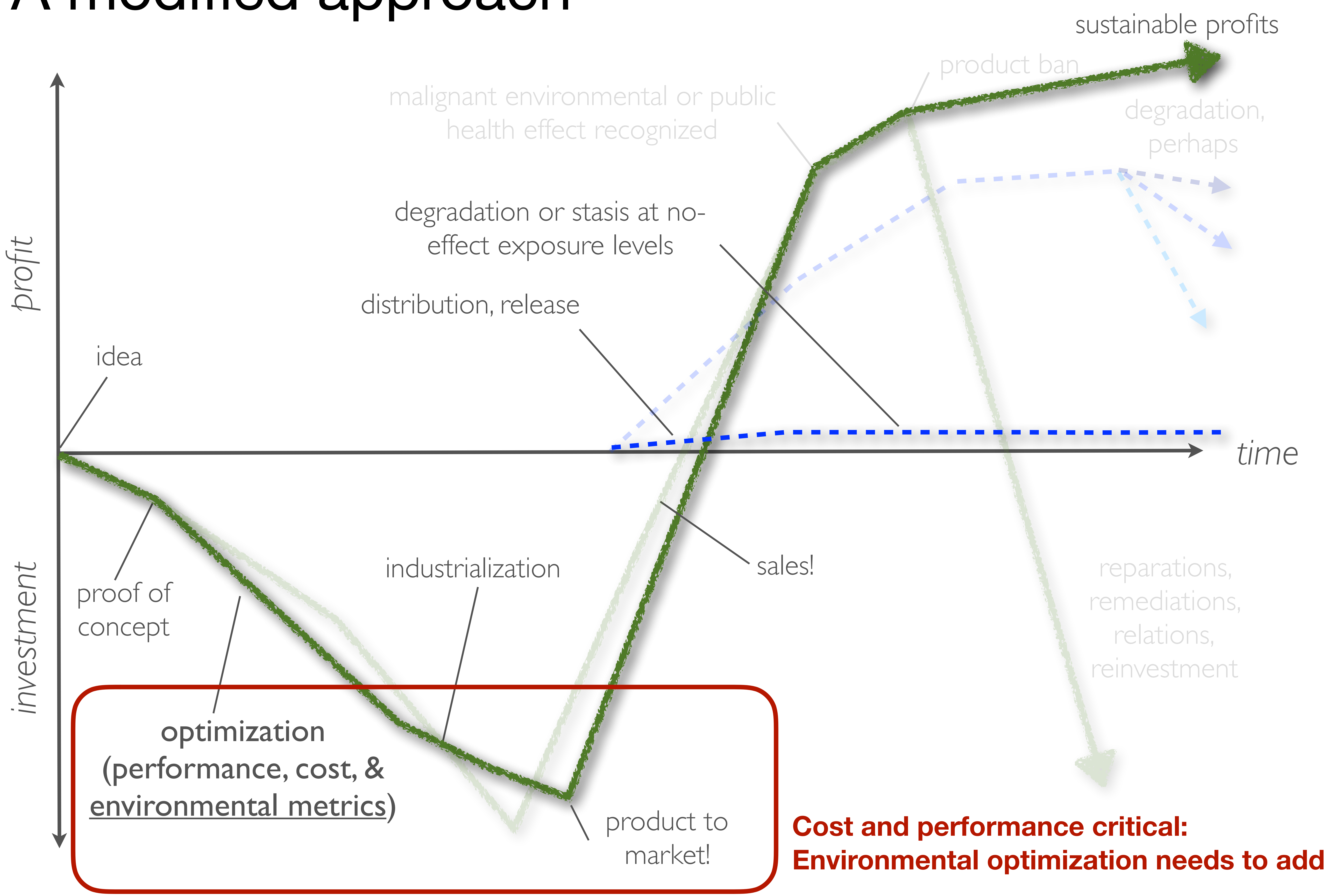

PRICE PER GALLON $
ALL TAXES INCLUDED
This Gasoline Contains up to:
15% MTBE
This Gasoline Contains up to:
10% Ethanol
xxon Plus
alamy stock photo



Status quo: Shortened product lifetimes & damage



A modified approach

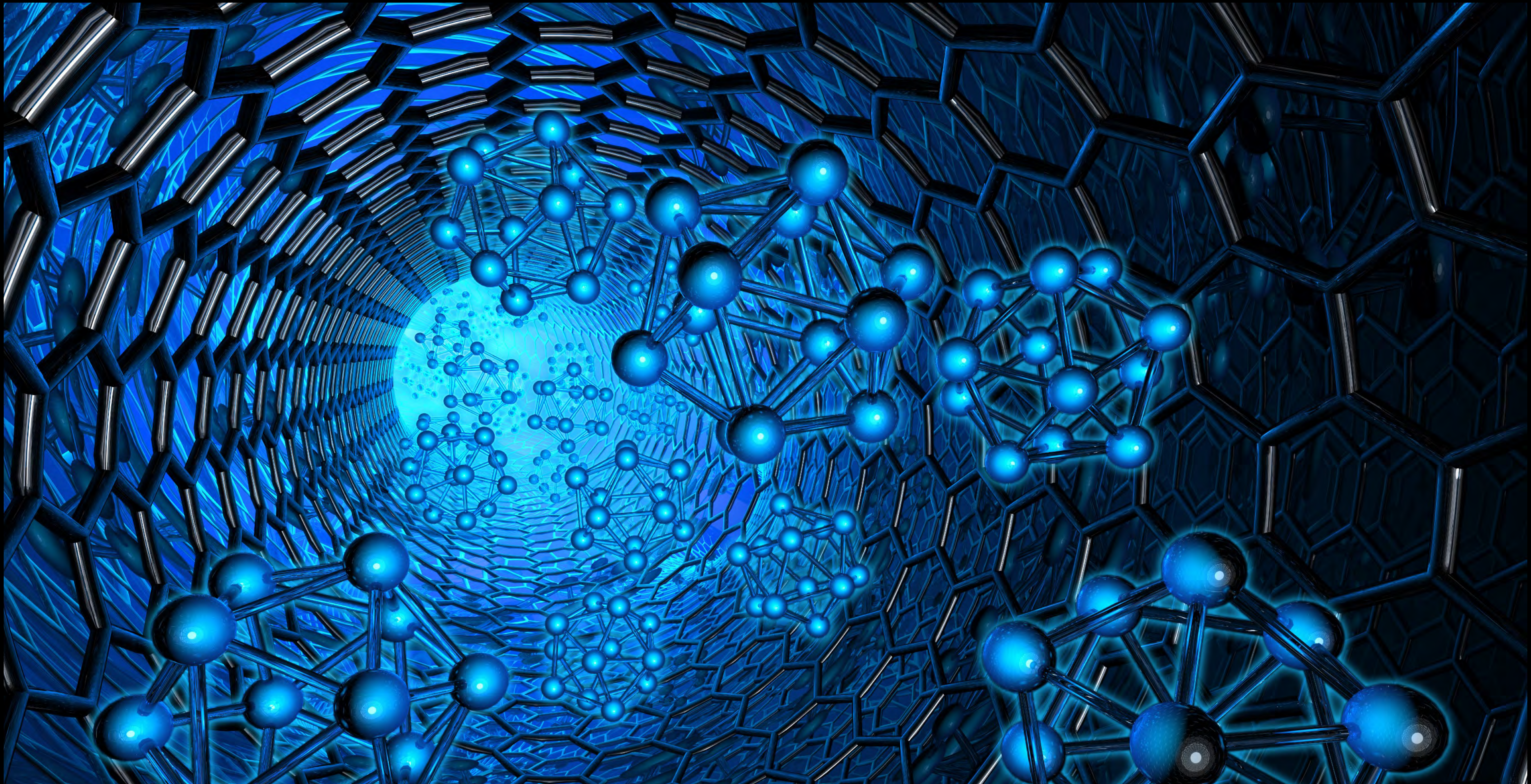


Cost and performance critical:
Environmental optimization needs to add value

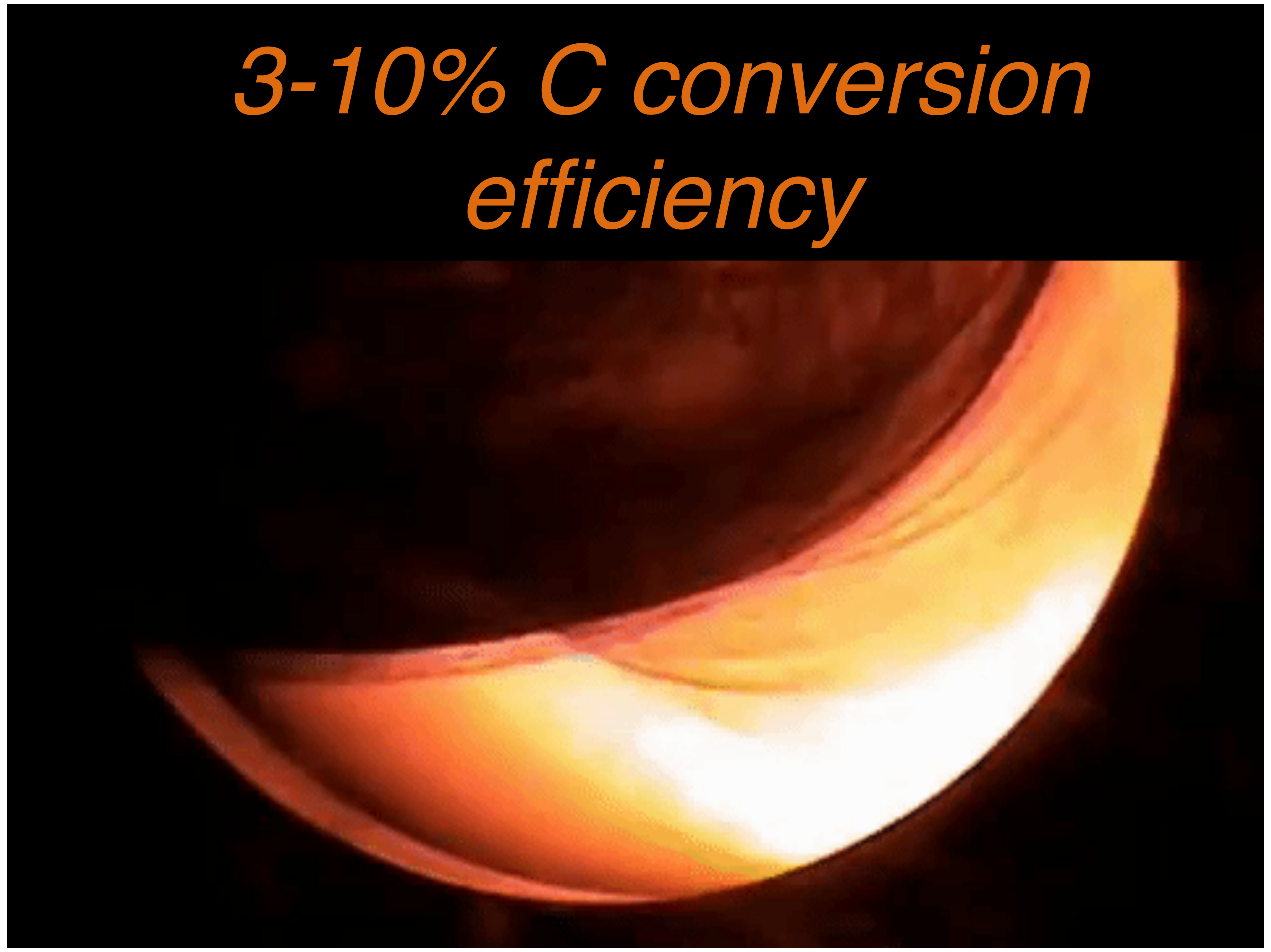
Disrupting highly complex manufacturing
and waste management systems

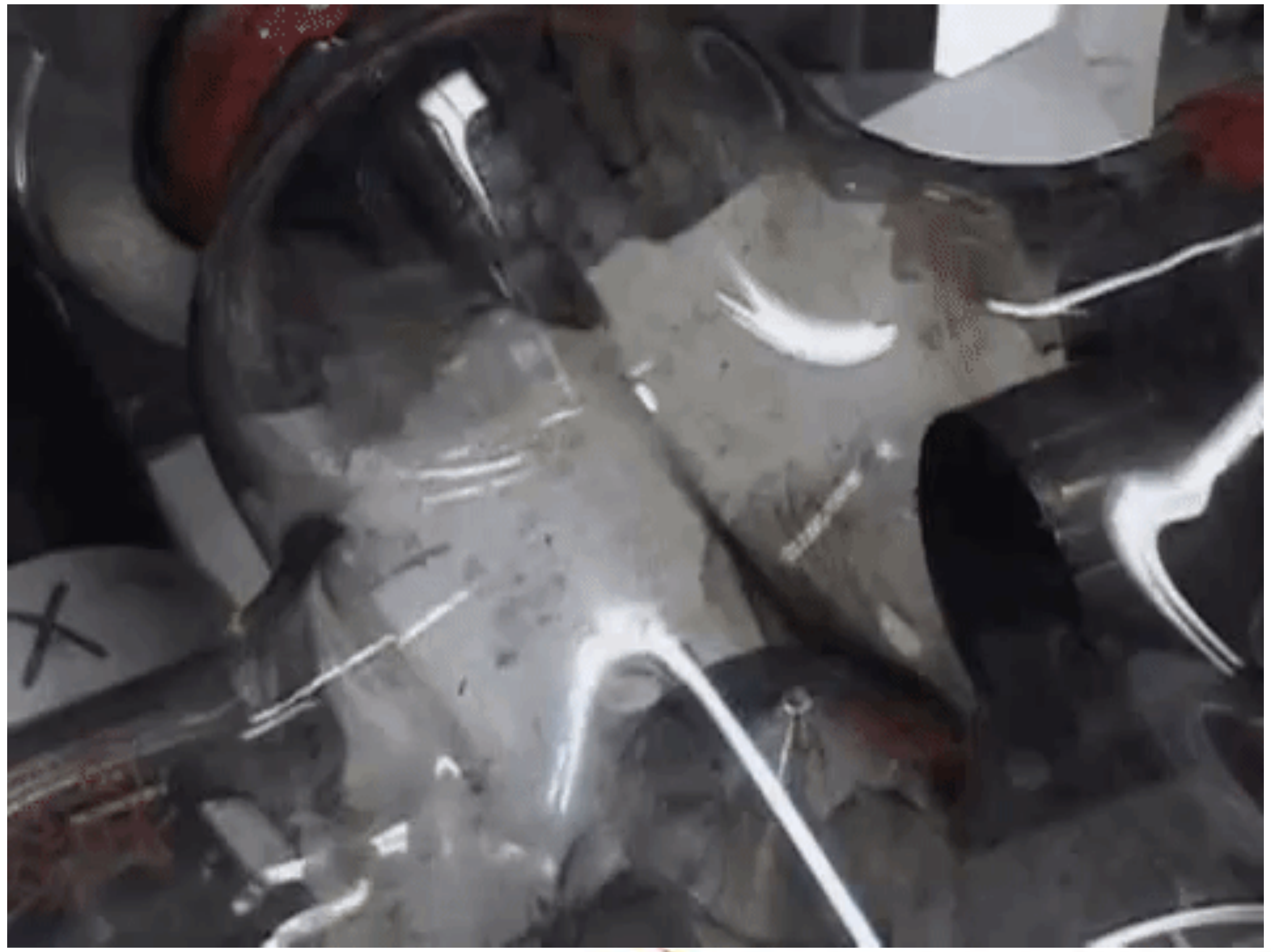
Nas ished industry,
Ea ep pace

NANOTECHNOLOGY



Large-scale CNT manufacture

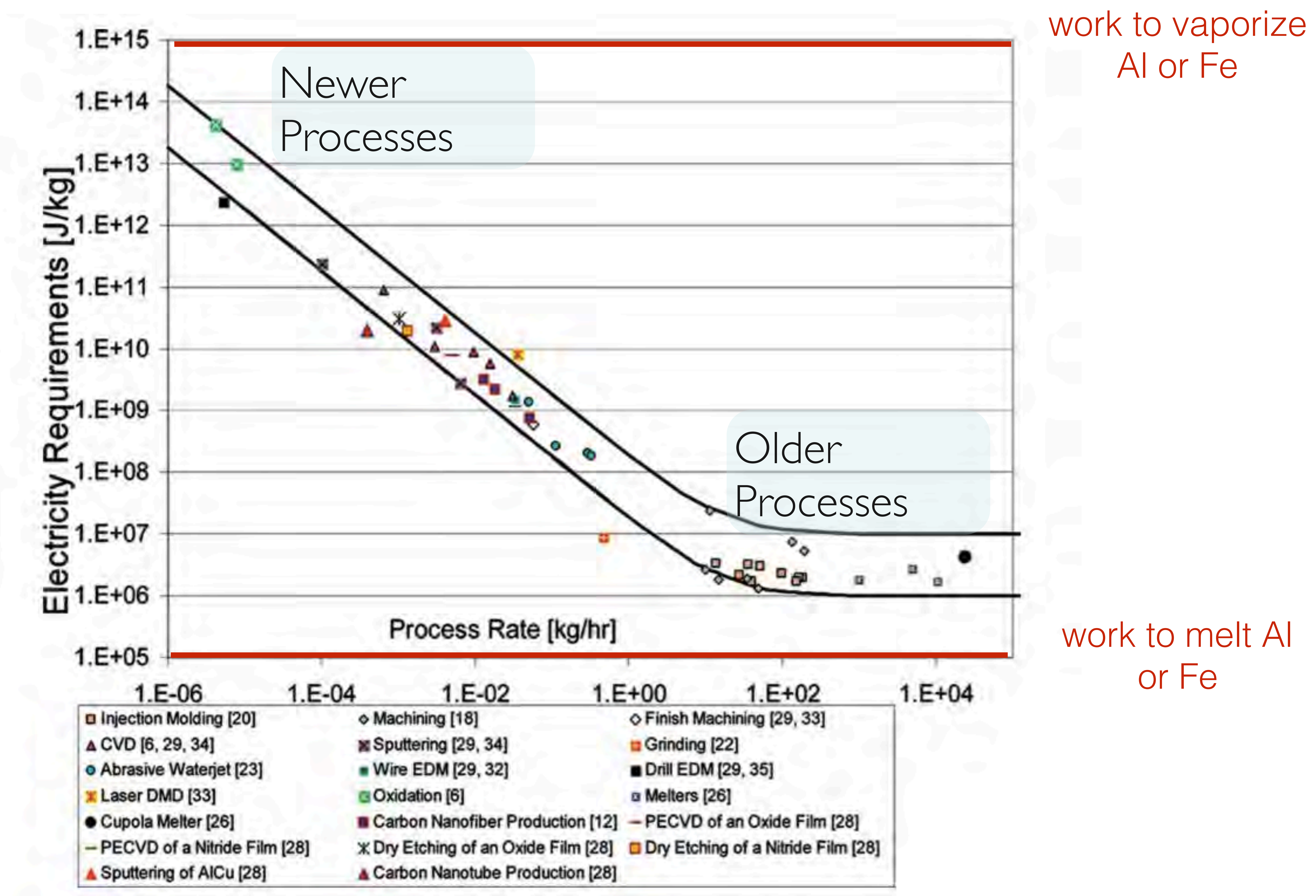




Healy et al. Industrial Ecology 2008

nanocomp
TECHNOLOGIES, INC.

Energy demands of most advanced processes are high…



Gutowski et al. Environ. Sci. Technol. 2009

...but reasonable considering small incorporated quantities

CNT payback time:
1 g CNTs storage device^{-1}~ 2.5 wks
1 kg CNTs device^{-1}~ 2 yrs

Some applications present a net energy **benefit**

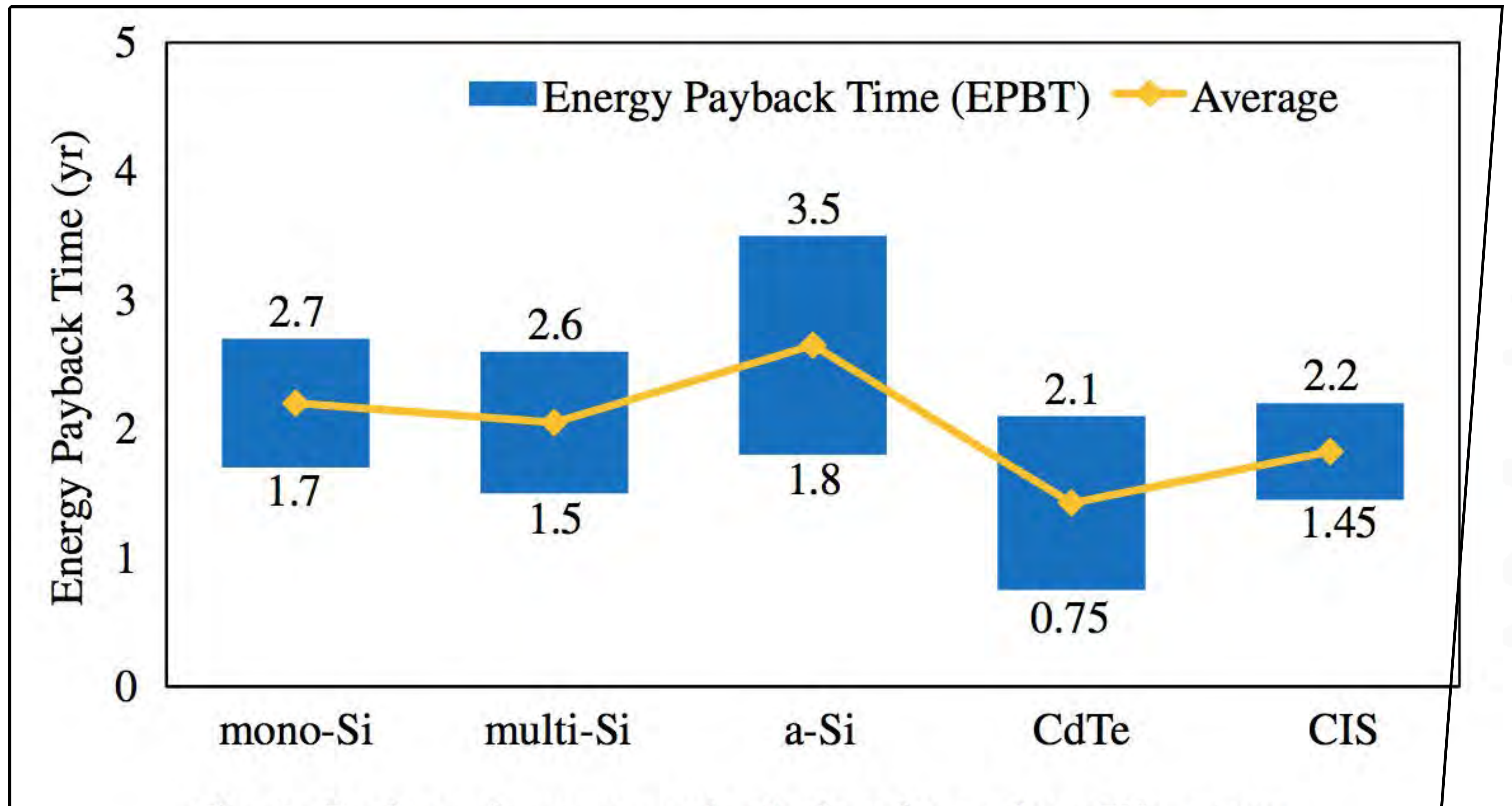
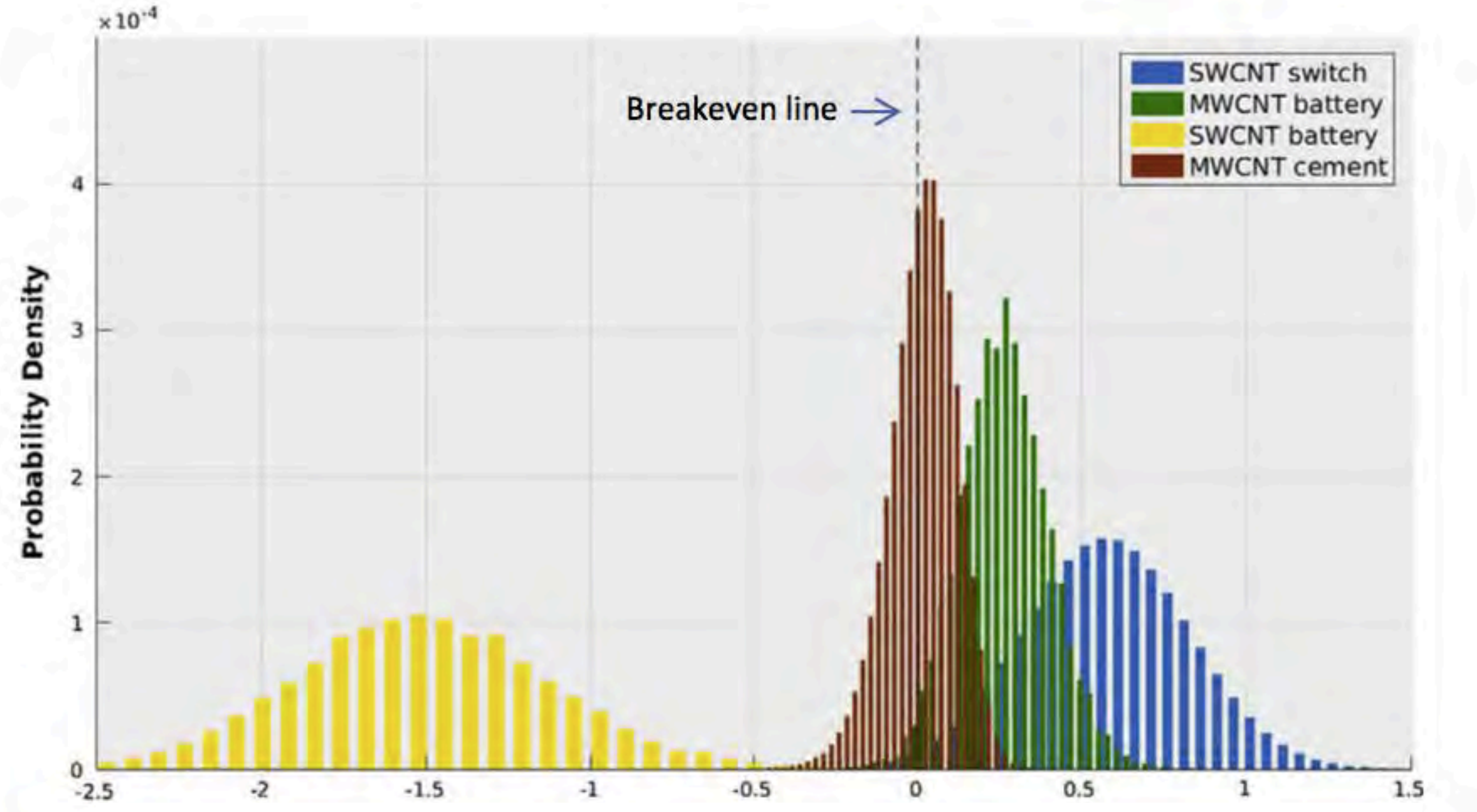


Fig. 5. Review of energy payback time for various PV systems.

Peng et al. Renewable & Sustainable Energy Reviews 2013



Net Energy Benefit (x 10^4 MJ = x 10 GJ)

Zhai et al. Applied Energy 2016

Nanotube synthesis among the most inefficient reactions of all time

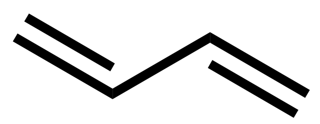
Industry sector	Annual production (t)	E-factor (waste-to-product ratio)	Waste produced (t)	# of steps	Years of development
Oil refining	10^6 - 10^8	ca. 0.1	10^5 - 10^7	separations	100+
Bulk chemicals					10 — 50
Fine chemicals					4 — 7
Pharma-ceuticals	10 - 10^3	25 — 100+	2.5×10^2 — 10^5	6+	3 — 5
CNTs	~2.2×10^3	~10-10^5	2.2×10^3 — 2.2×10^8	1-3	~10-25

Quick & dirty:
2,200 ton/yr CNT production (DeVolder et al. 2013)
7 kton/yr - 0.22 Gton/yr?!

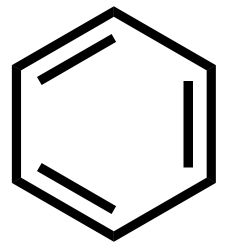
R. A. Sheldon, Chem. Ind. (London), 1992, 903–906.
DeVolder et al. Science 2013; Eckelman et al. 2008; Anastas

Unsavory emissions

Volatile organic compounds (VOCs)

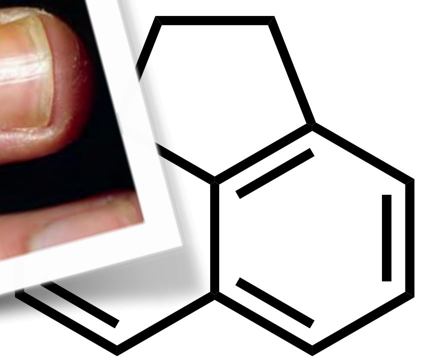


1,3-butadiene

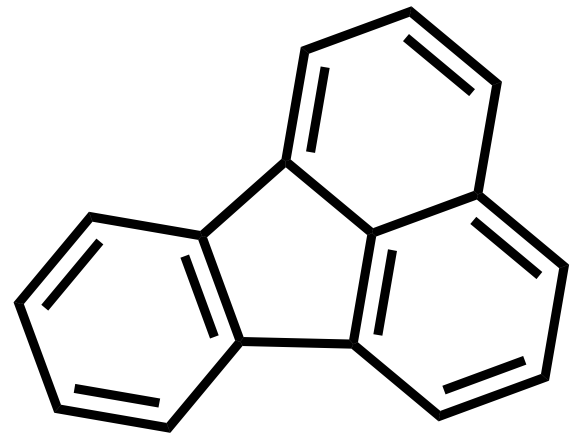


benzene

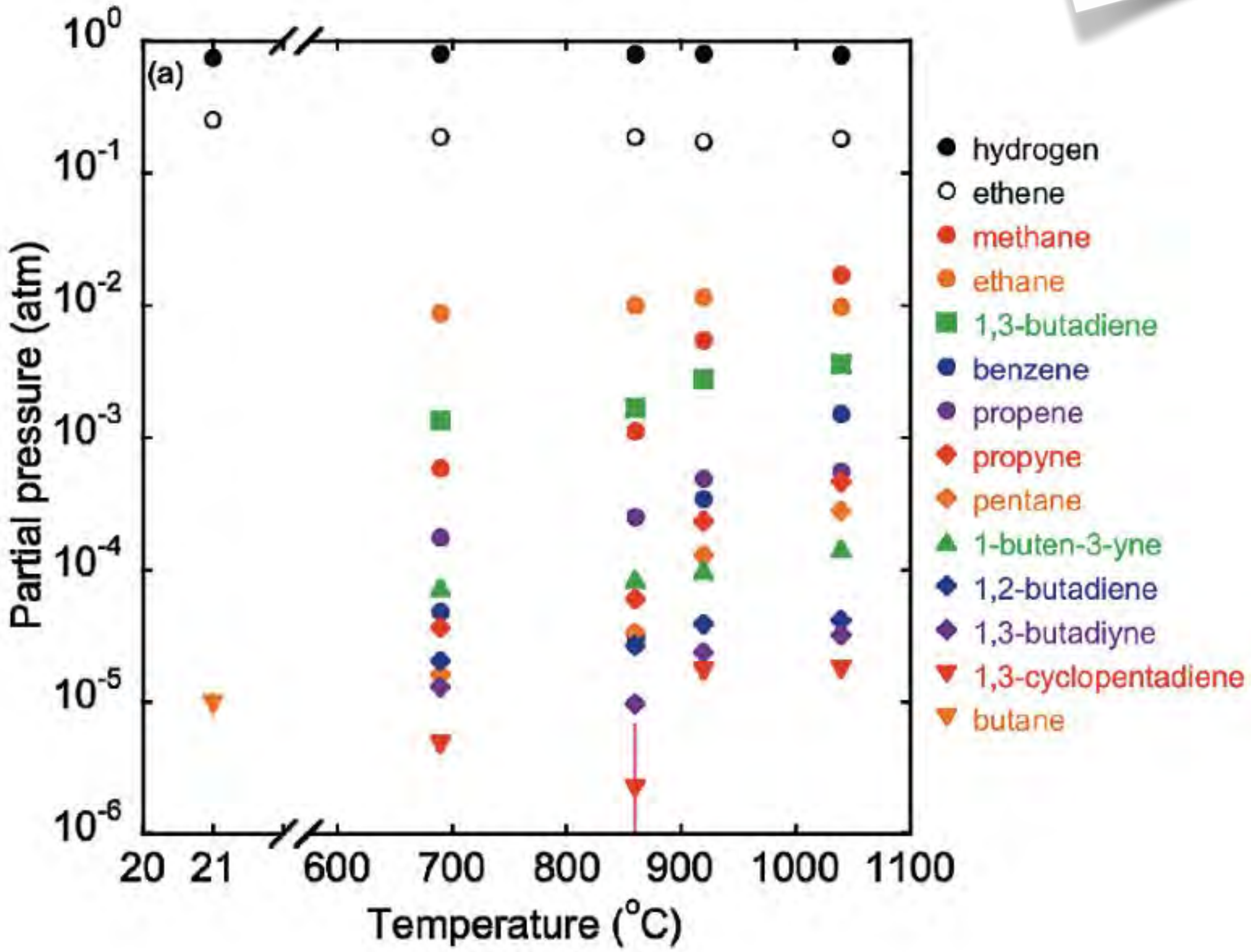
Polycyclic aromatic hydrocarbons (PAHs)

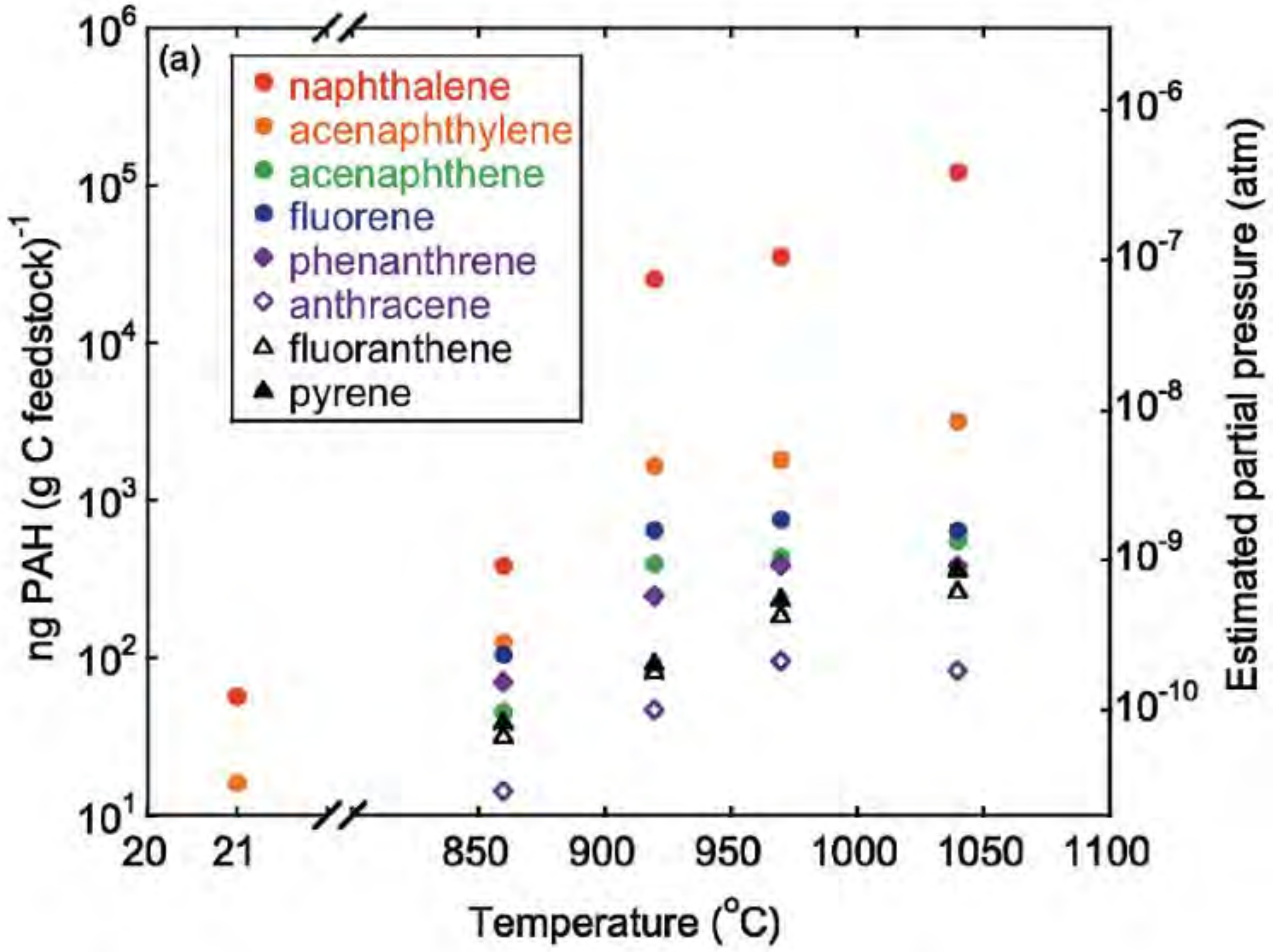


acenaphthene



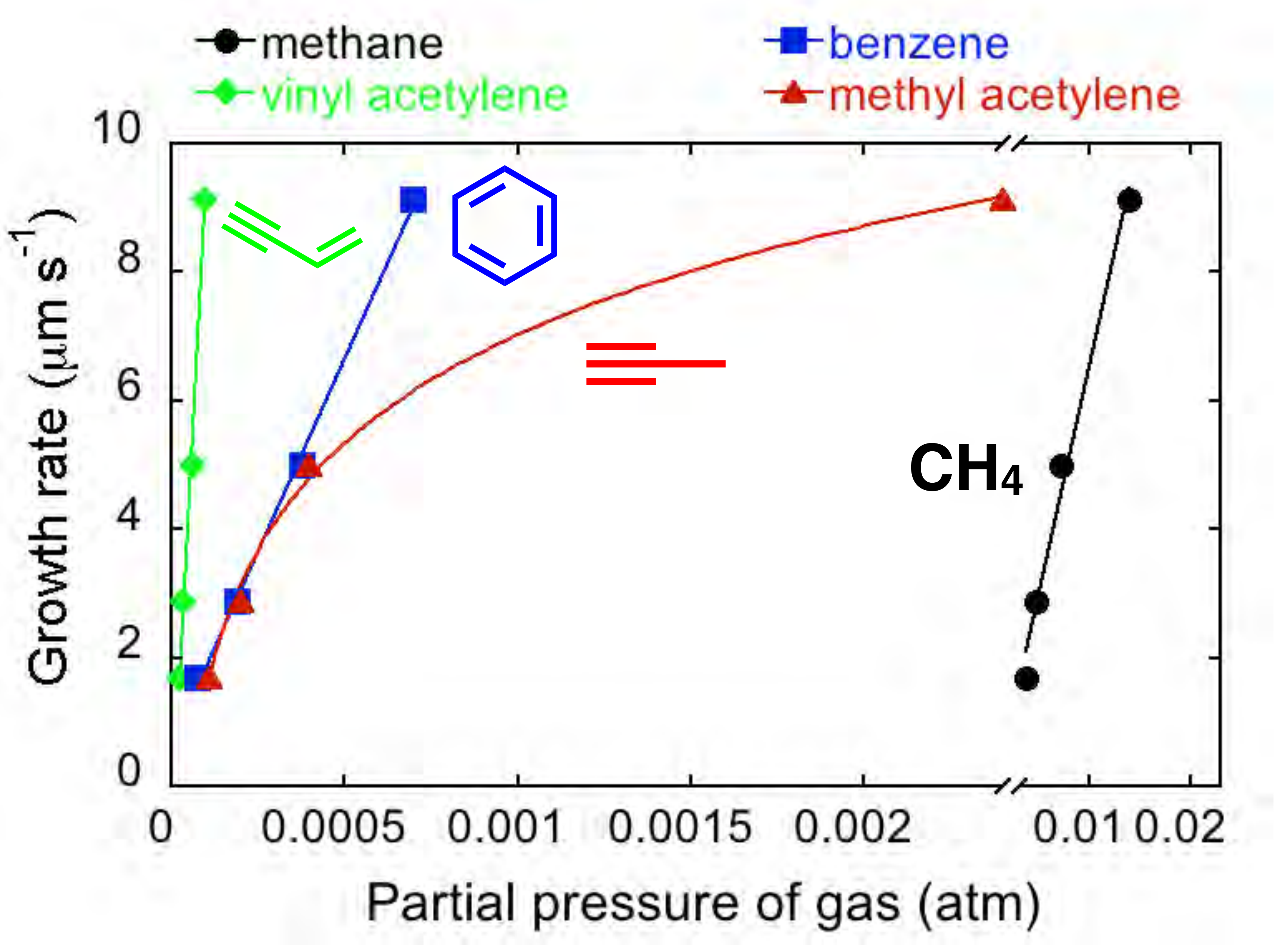
fluoranthene

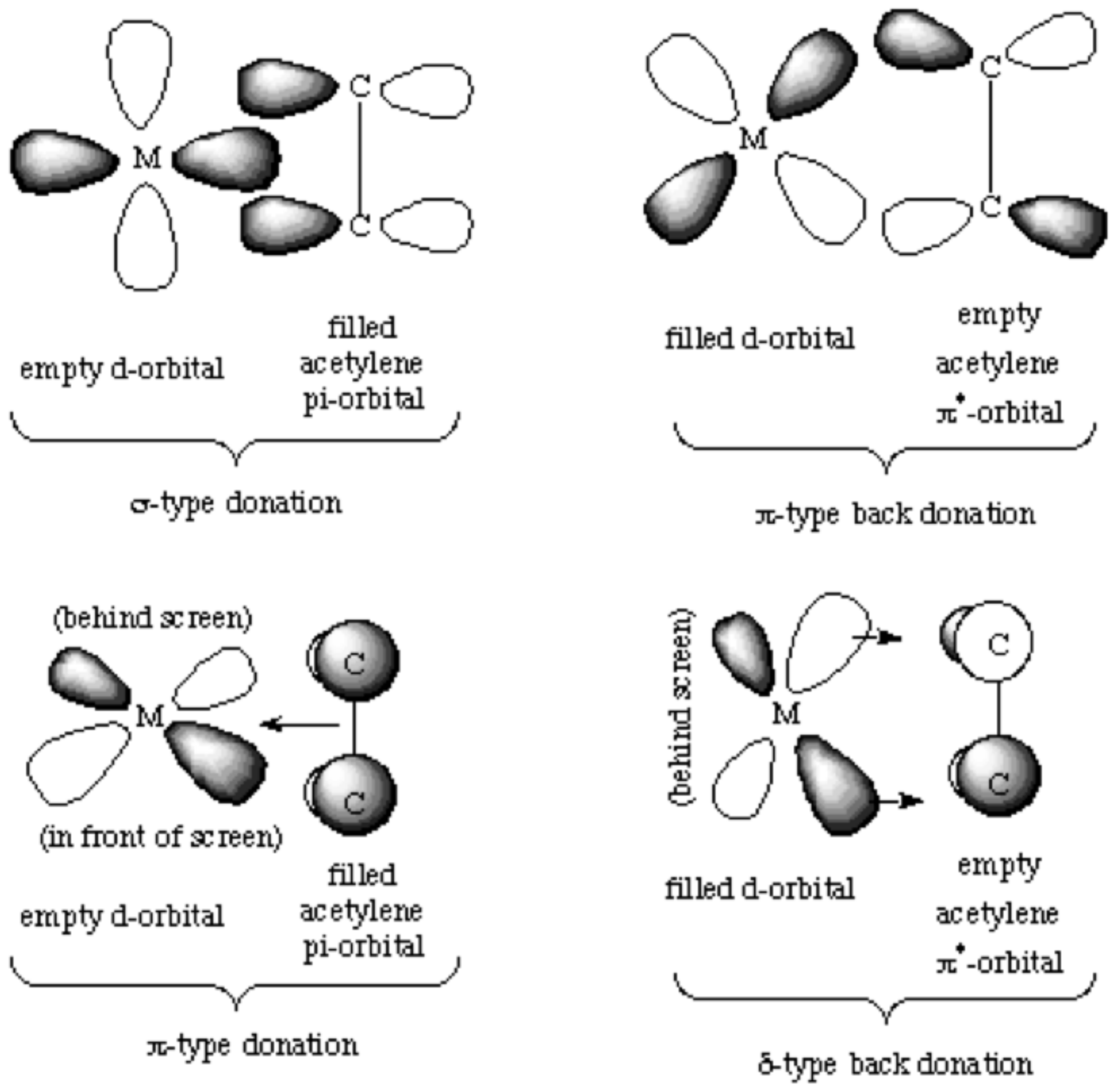




Plata et al. Environ. Sci. Technol. 2009

Emissions are just reaction products



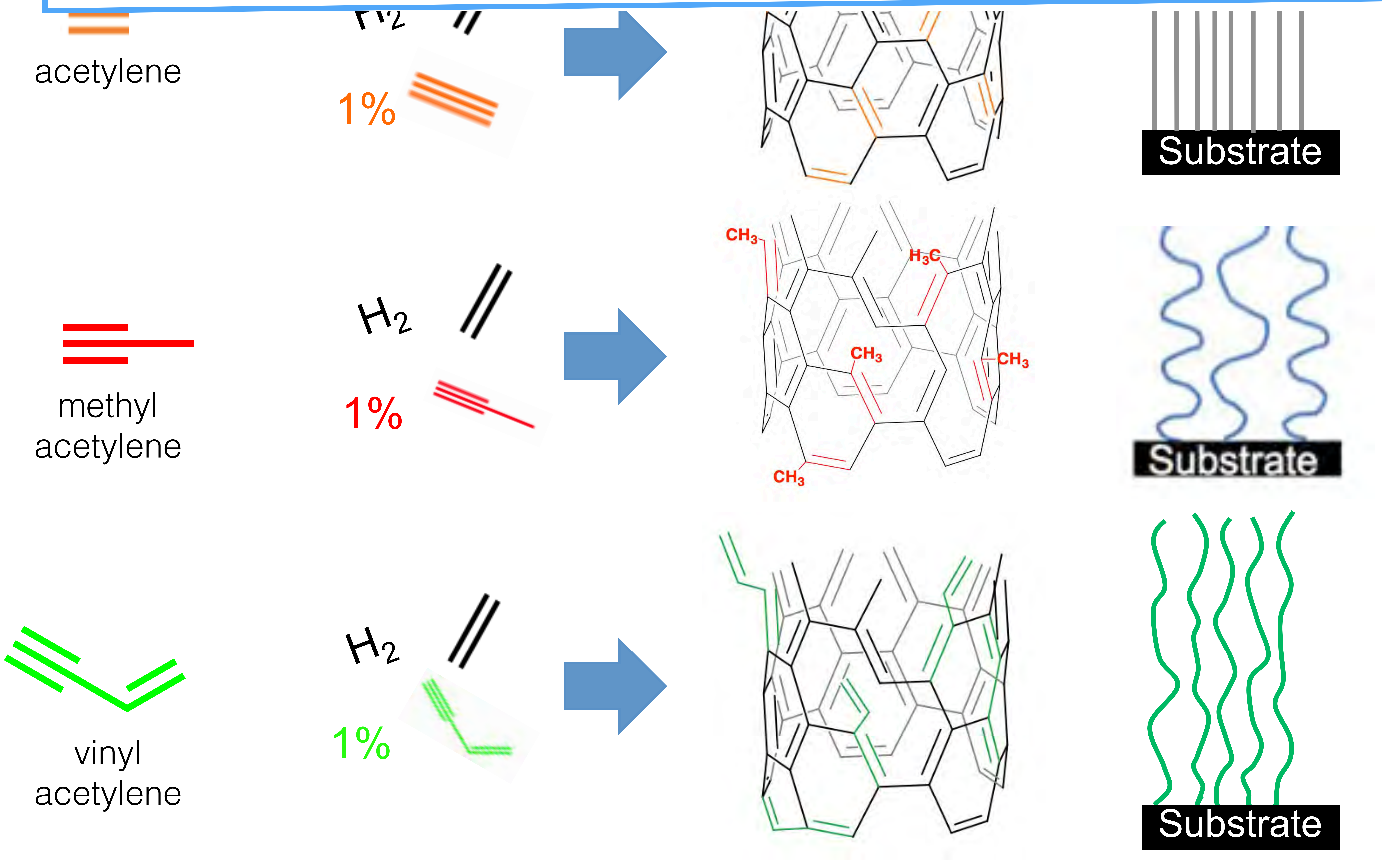


Plata et al. Environ. Sci. and Tech. 2009
Plata et al. ACS Nano 2010

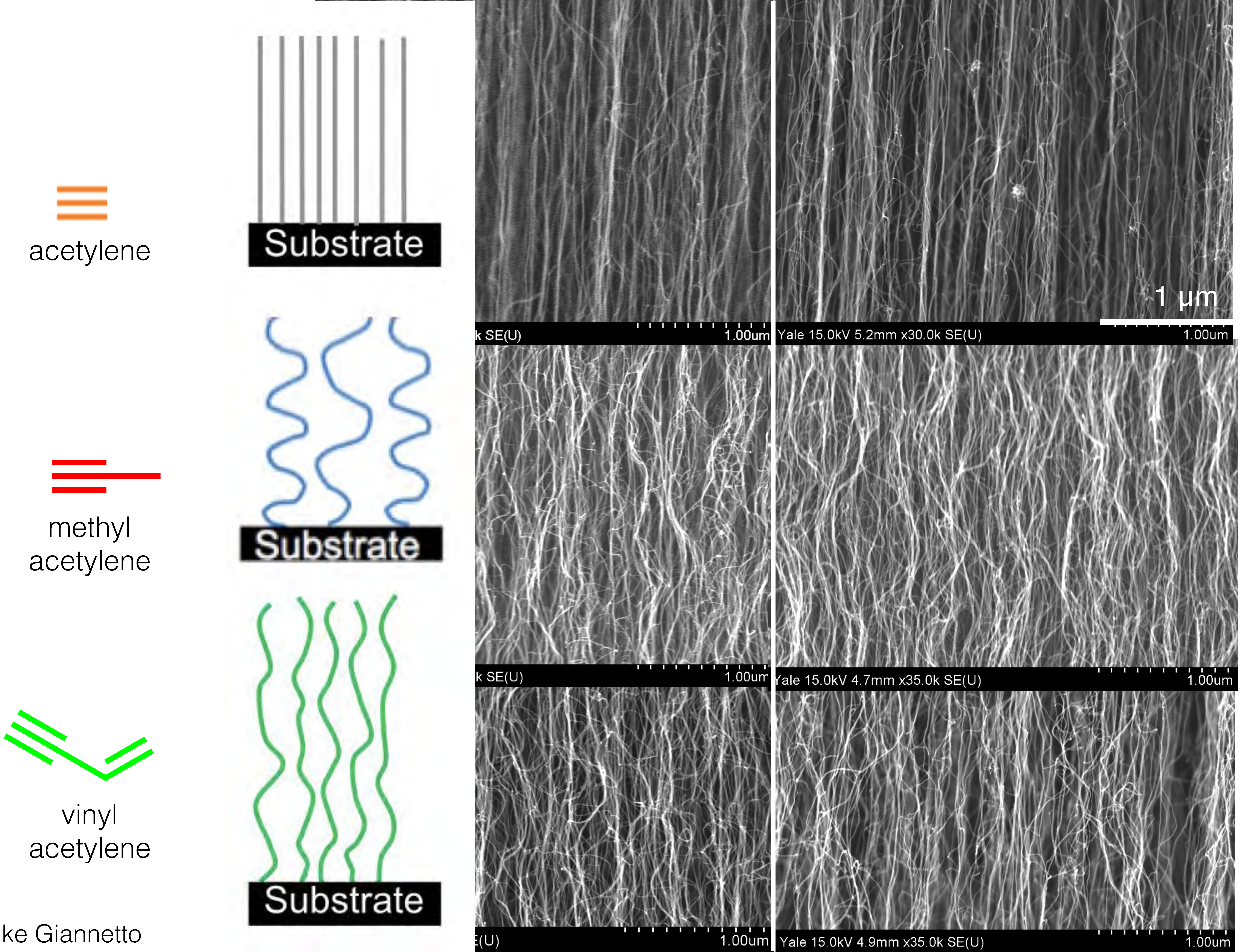
Mixed model:

if R lacks π bonds, then R group persists;

if R includes π bonds; R group may form a ring or persist

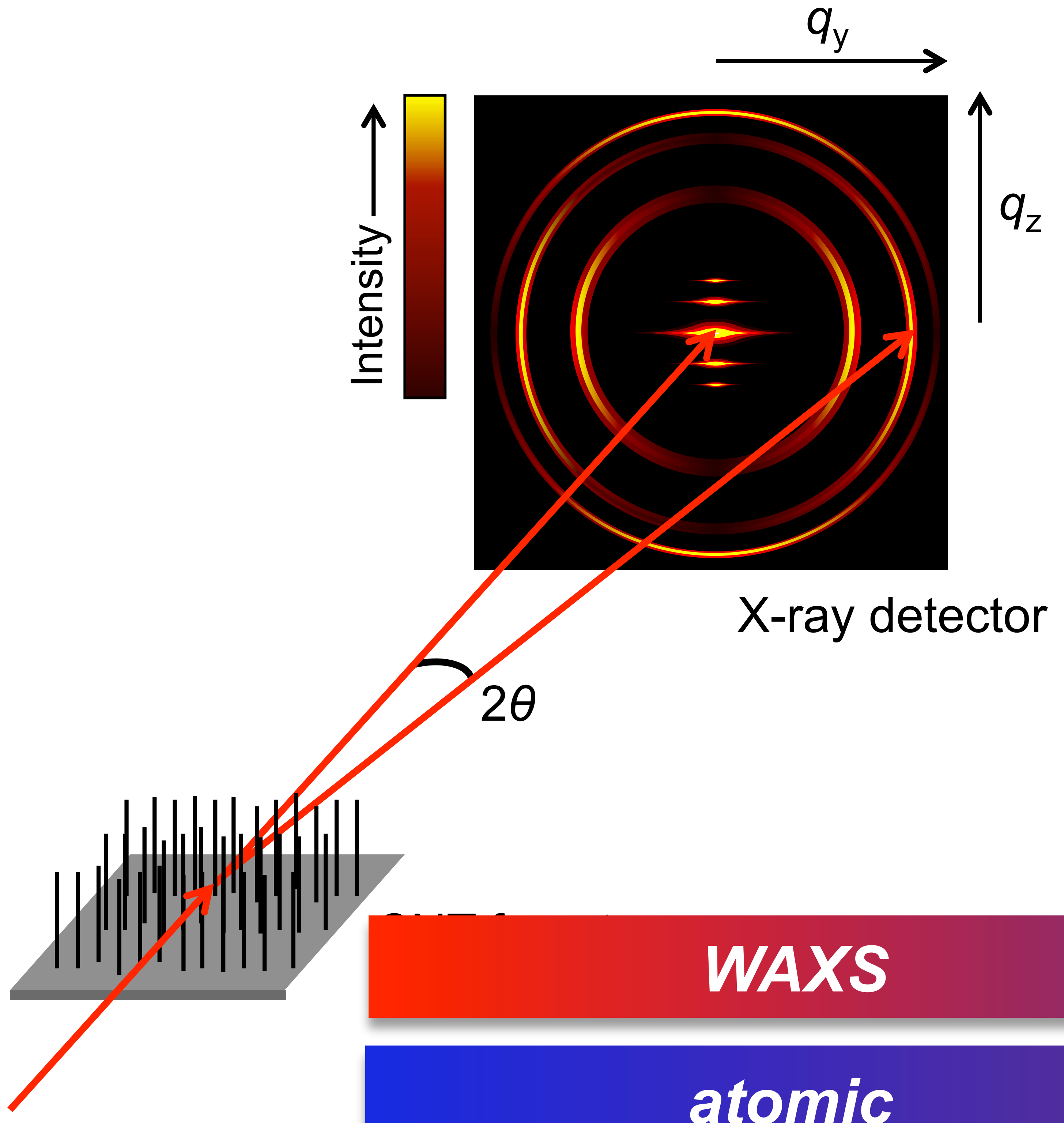


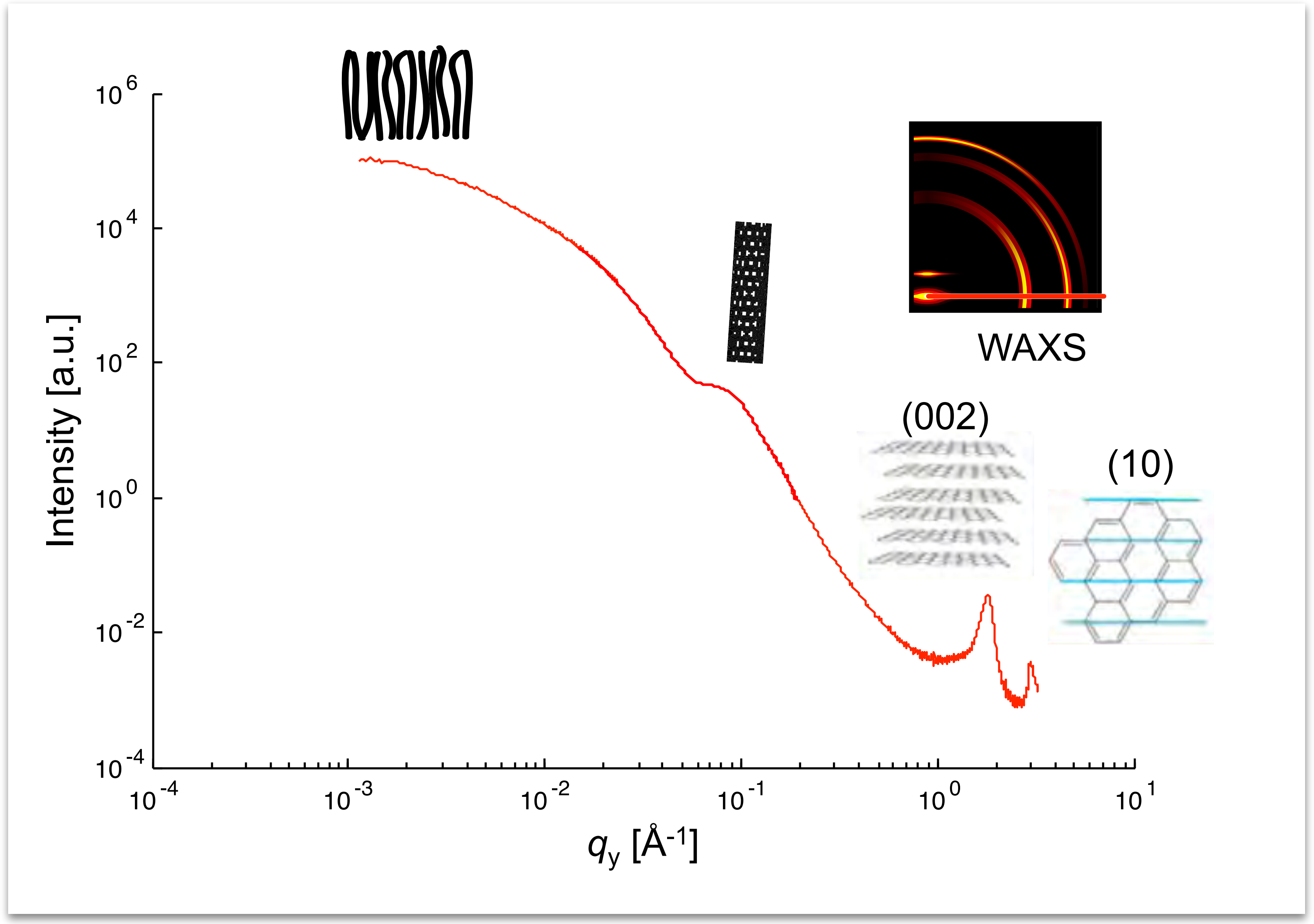
Mike Giannetto



Mike Giannetto

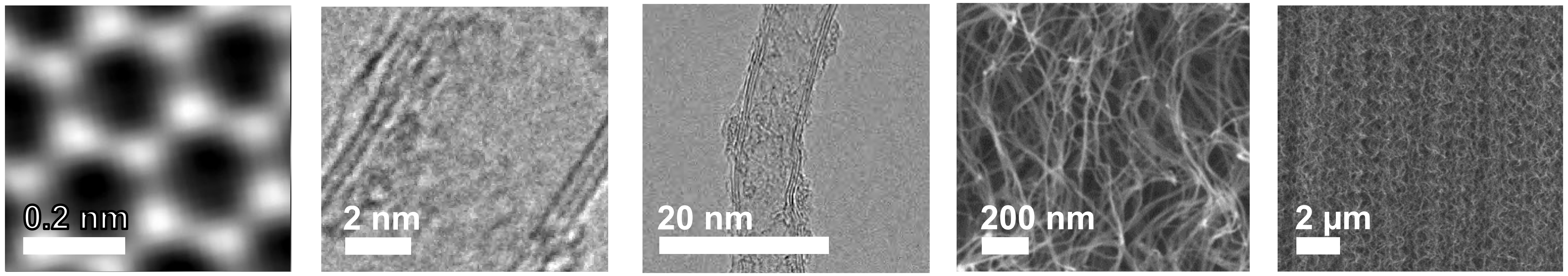
Molecular feature diagnostics via x-ray scattering





WAXS ***SAXS*** ***RSOXS (USAXS)***

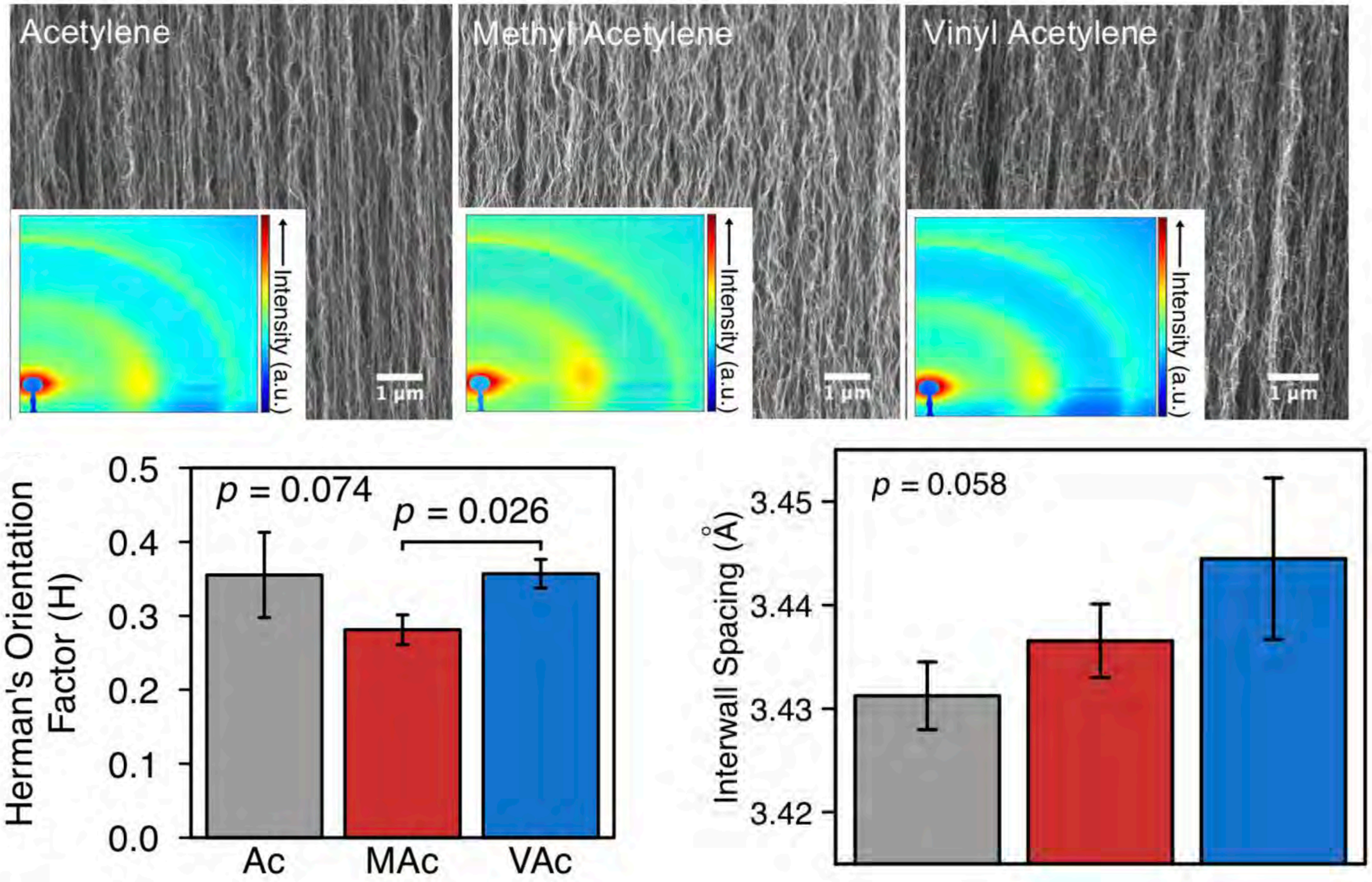
atomic ***nano*** ***meso*** ***micro***



Eric Meshot (Lawrence Livermore National Laboratory)

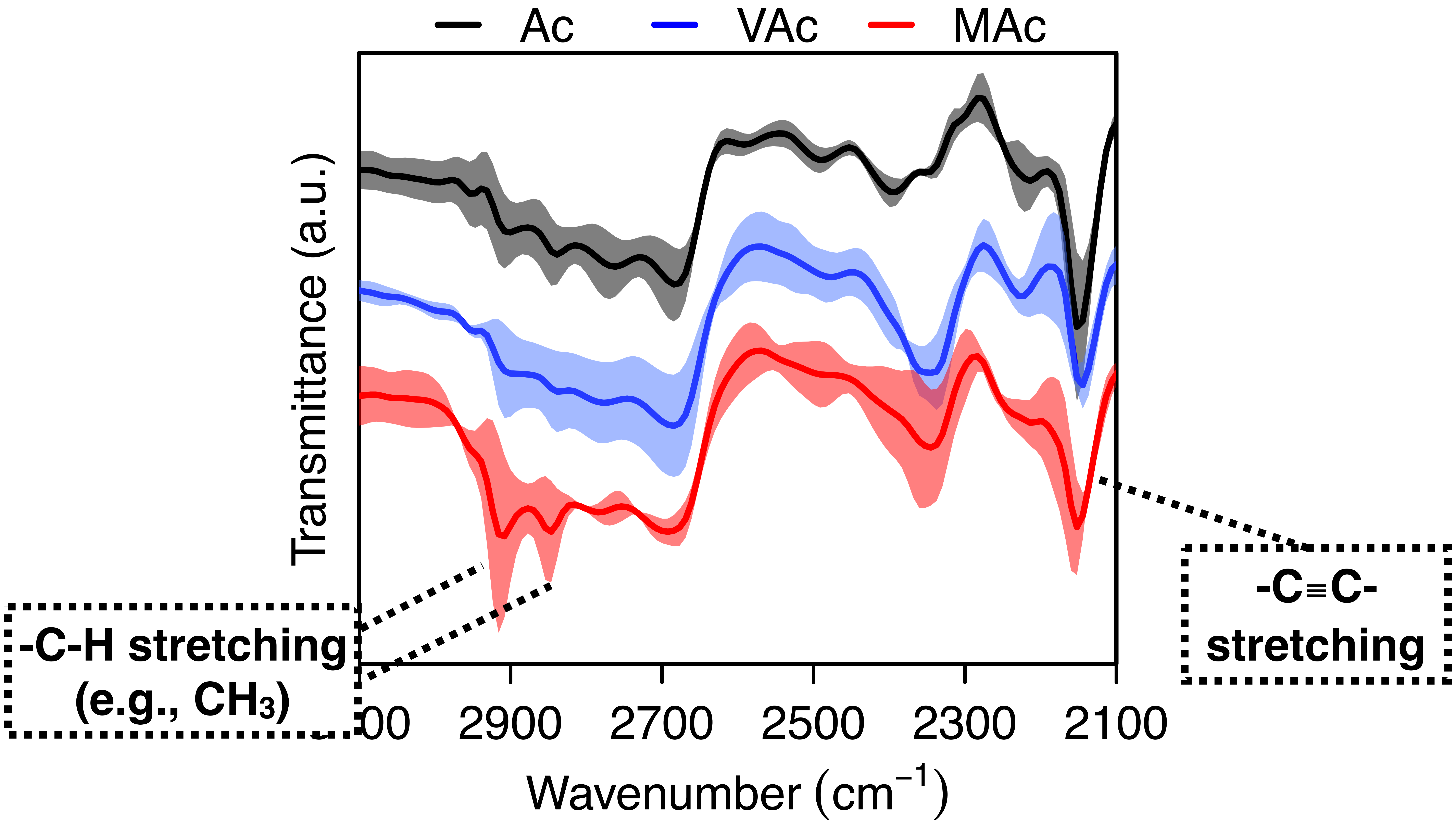
Faber et al. JPCC 2014

Alignment and inter tube spacing are distinct: Structures intact during incorporation!



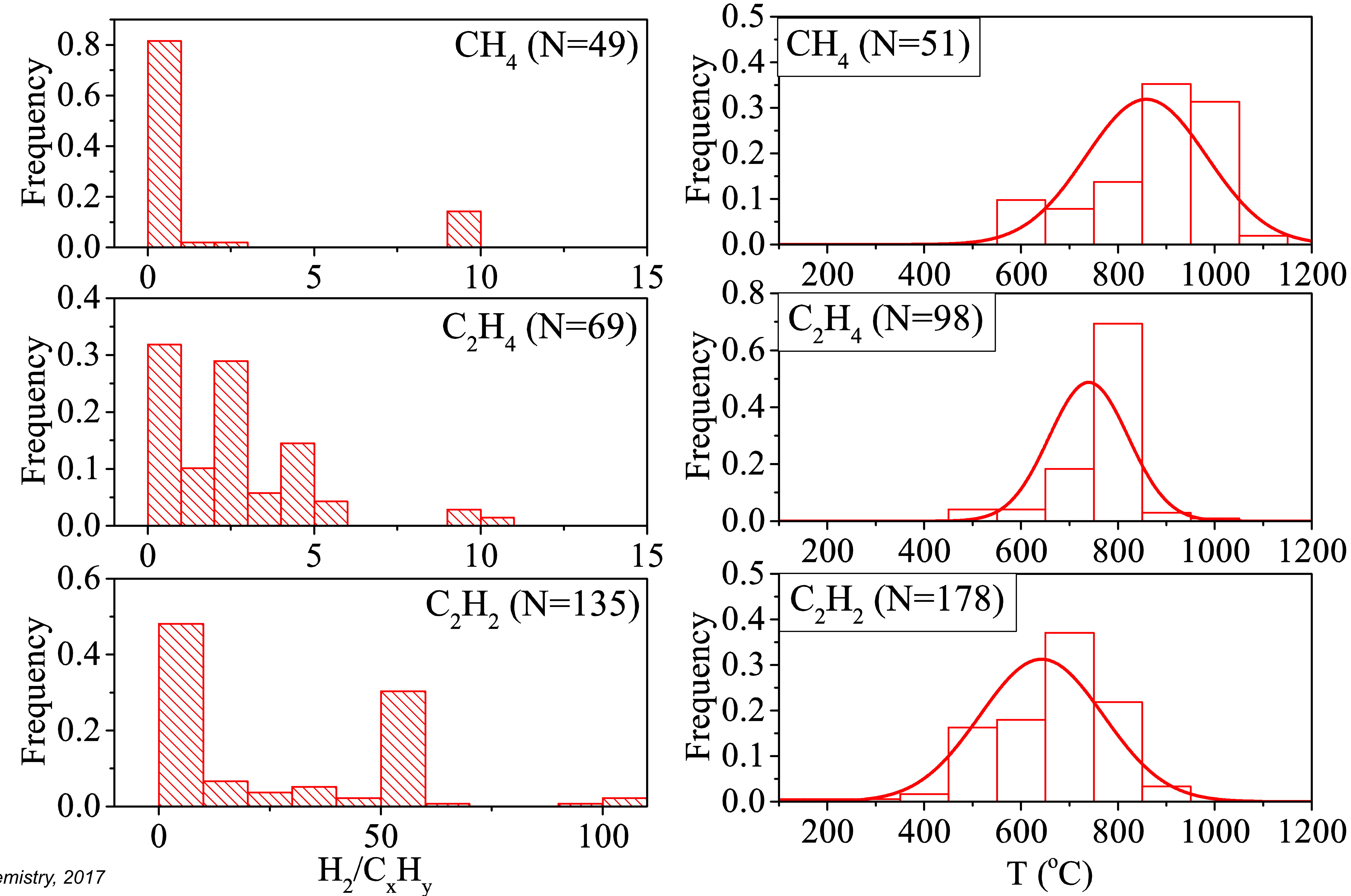
Mike Giannetto, Adam Watson, Eric Meshot, Eric Johnson, Edgar Dimitrov, Desiree Plata, Unpublished

Methyl side group persists!
(and other wild things)



Mike Giannetto, Eric Johnson, Desiree Plata, Unpublished

The importance of alkynes born out in the literature

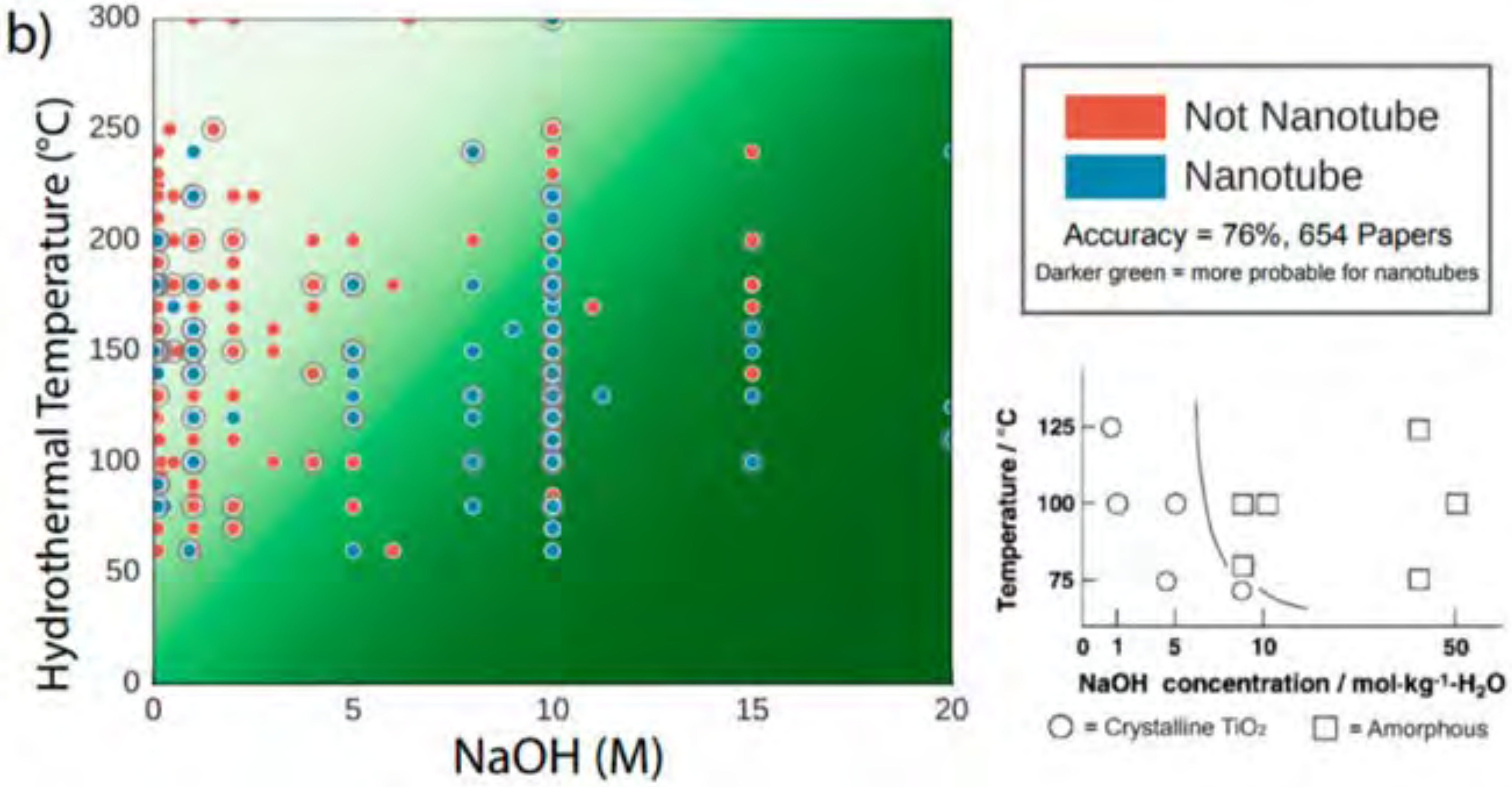


Shi, Plata et al. Green Chemistry, 2017

Computer-assisted process optimization

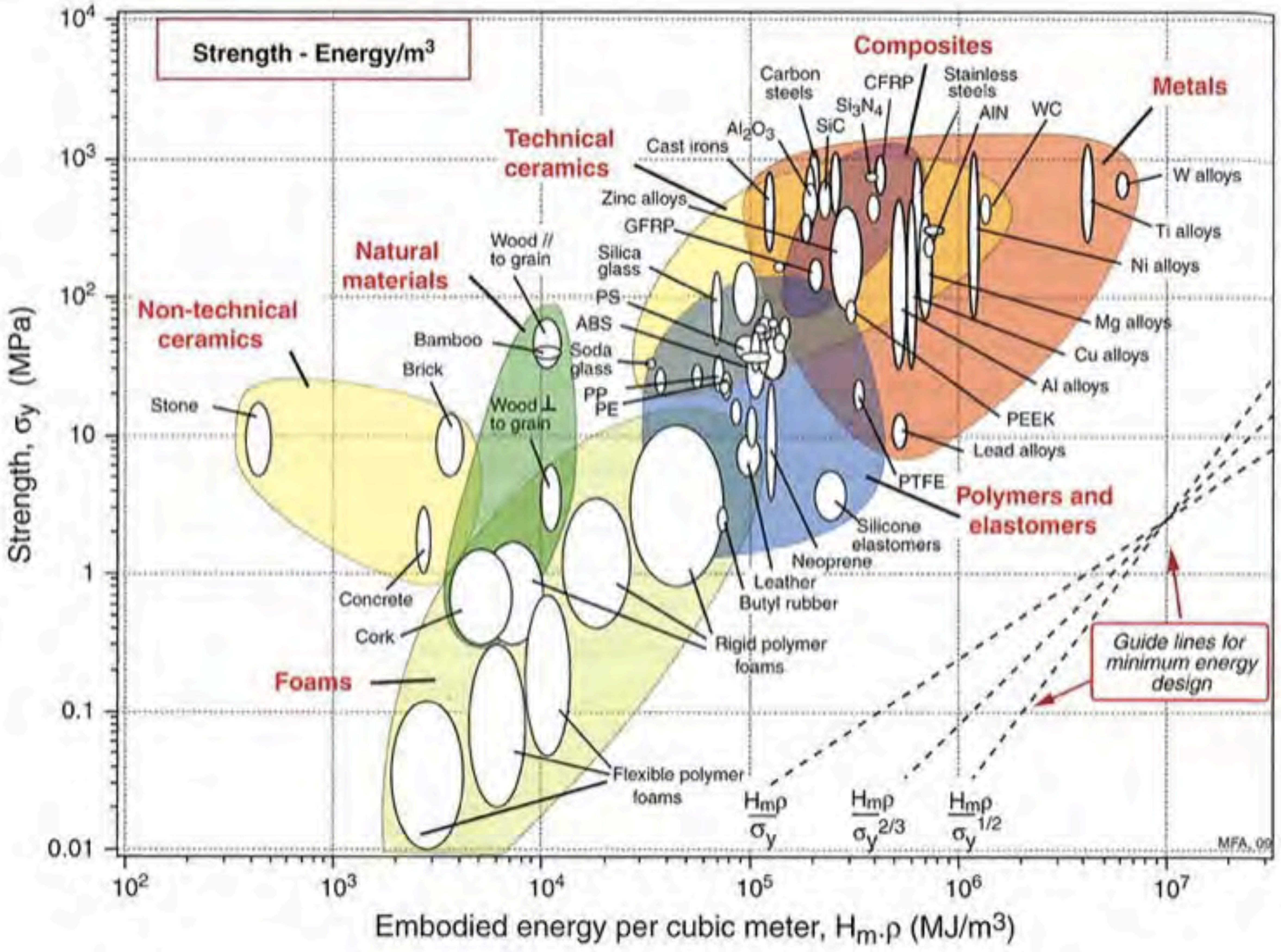
Materials Synthesis Insights from Scientific Literature via Text Extraction and Machine Learning

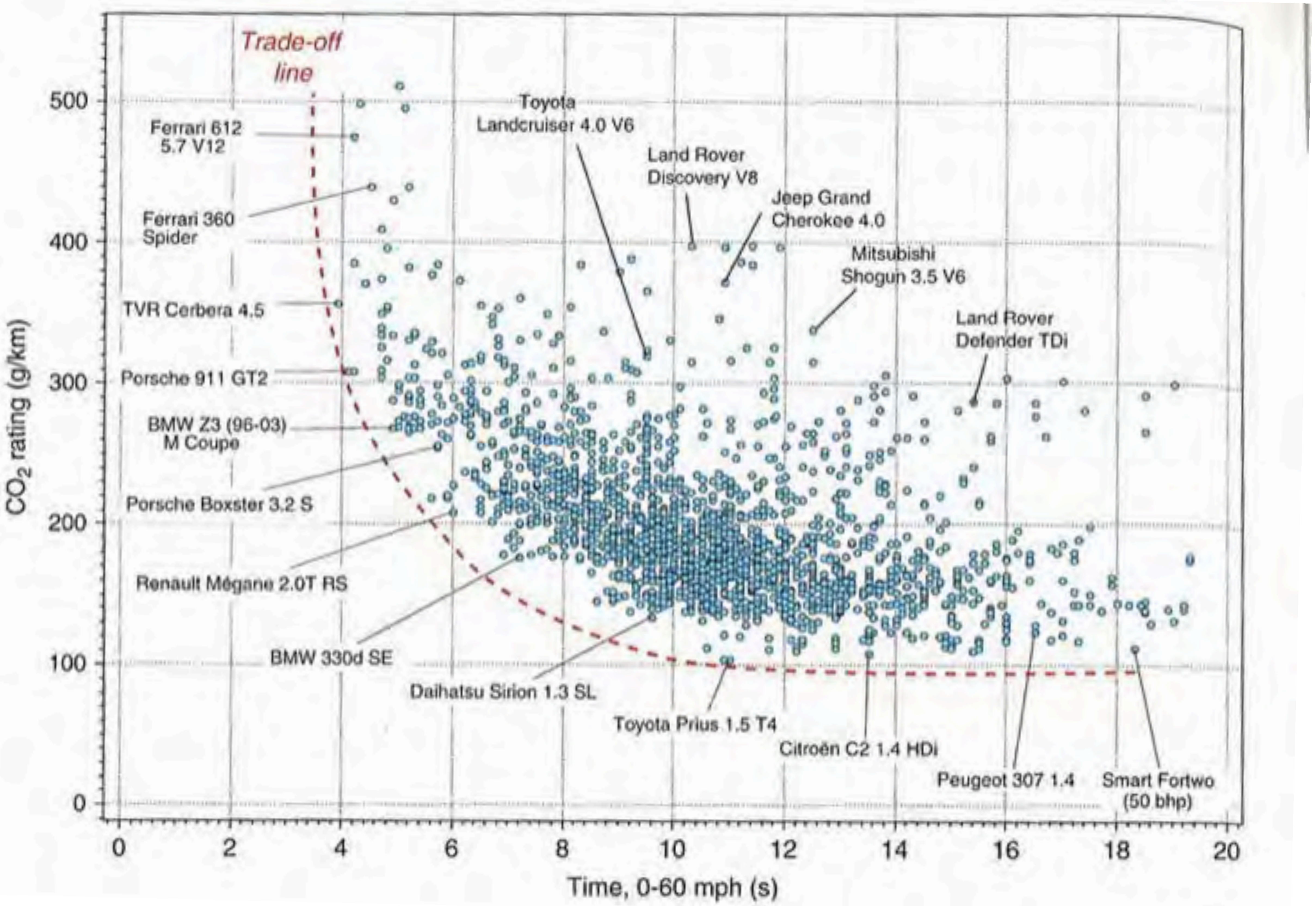
Edward Kim, Kevin Huang, Adam Saunders, Andrew McCallum, Gerbrand Ceder, and Elsa Olivetti*



Chemistry of Materials, 2017

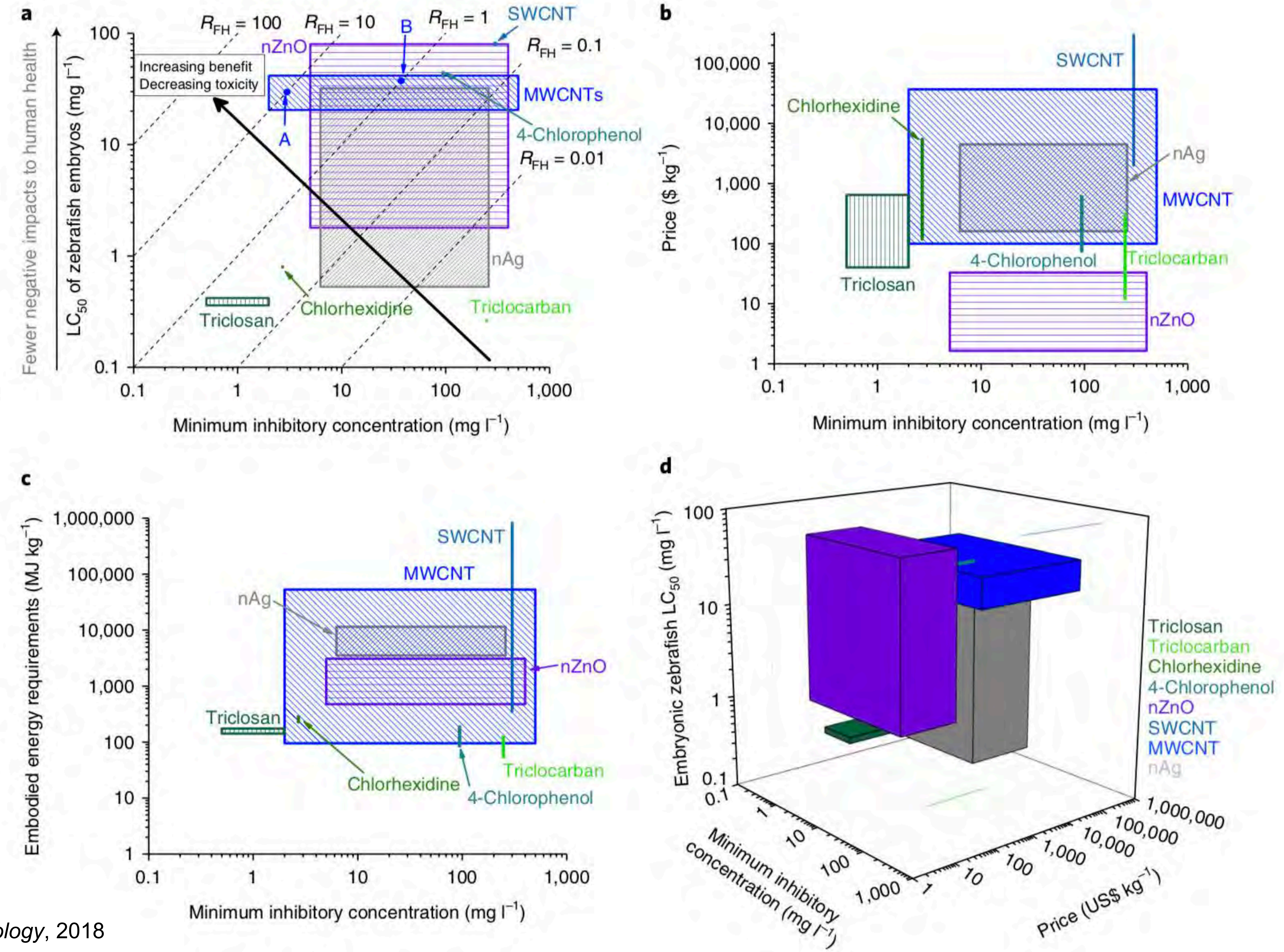
Incorporating environmental metrics into traditional materials selection schema





Ashby, Materials in the Environment, 2009

Simultaneous optimization via Ashby material selection diagrams: Navigating the material space

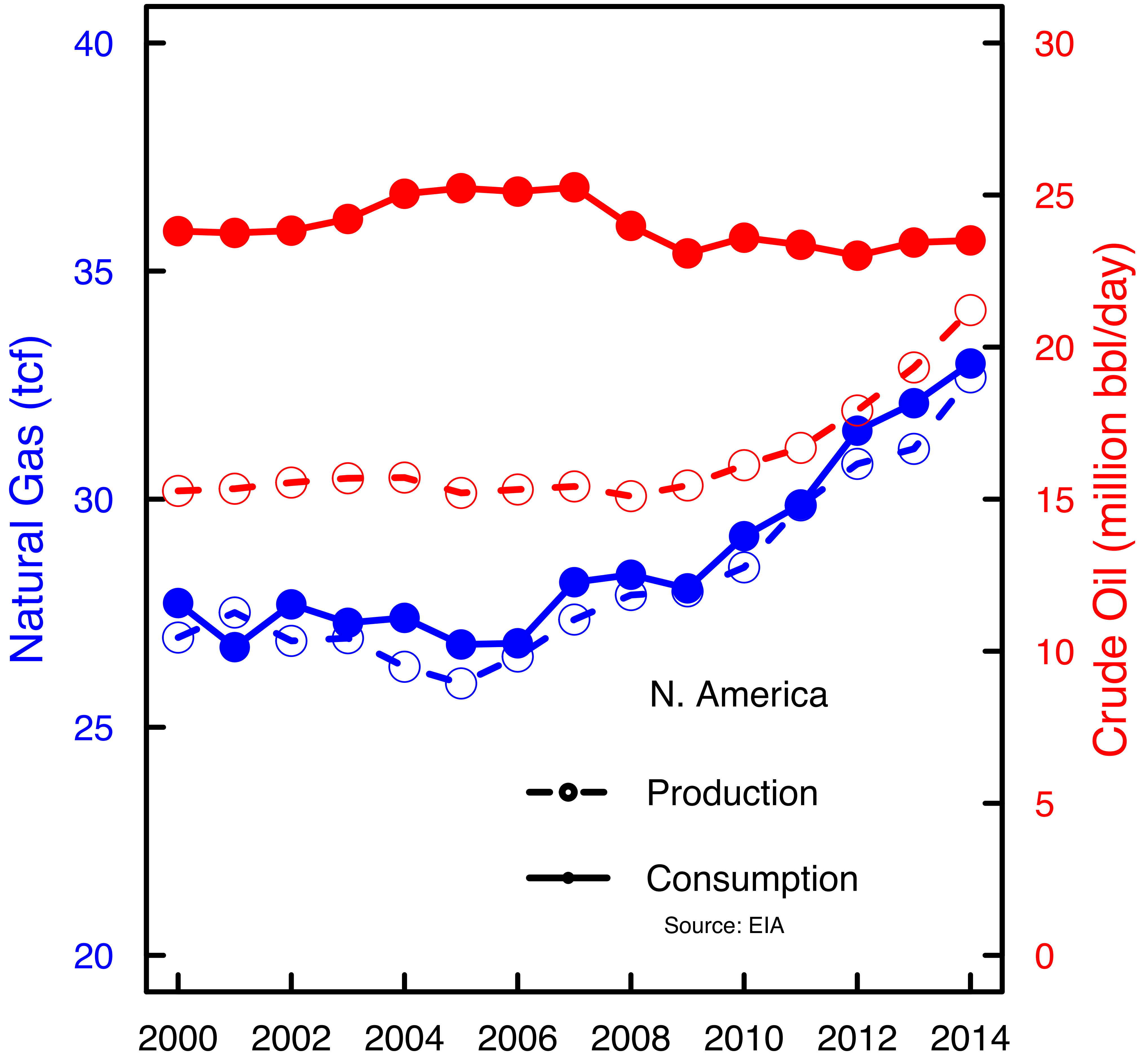


Falinski, Plata et al. *Nature Nanotechnology*, 2018

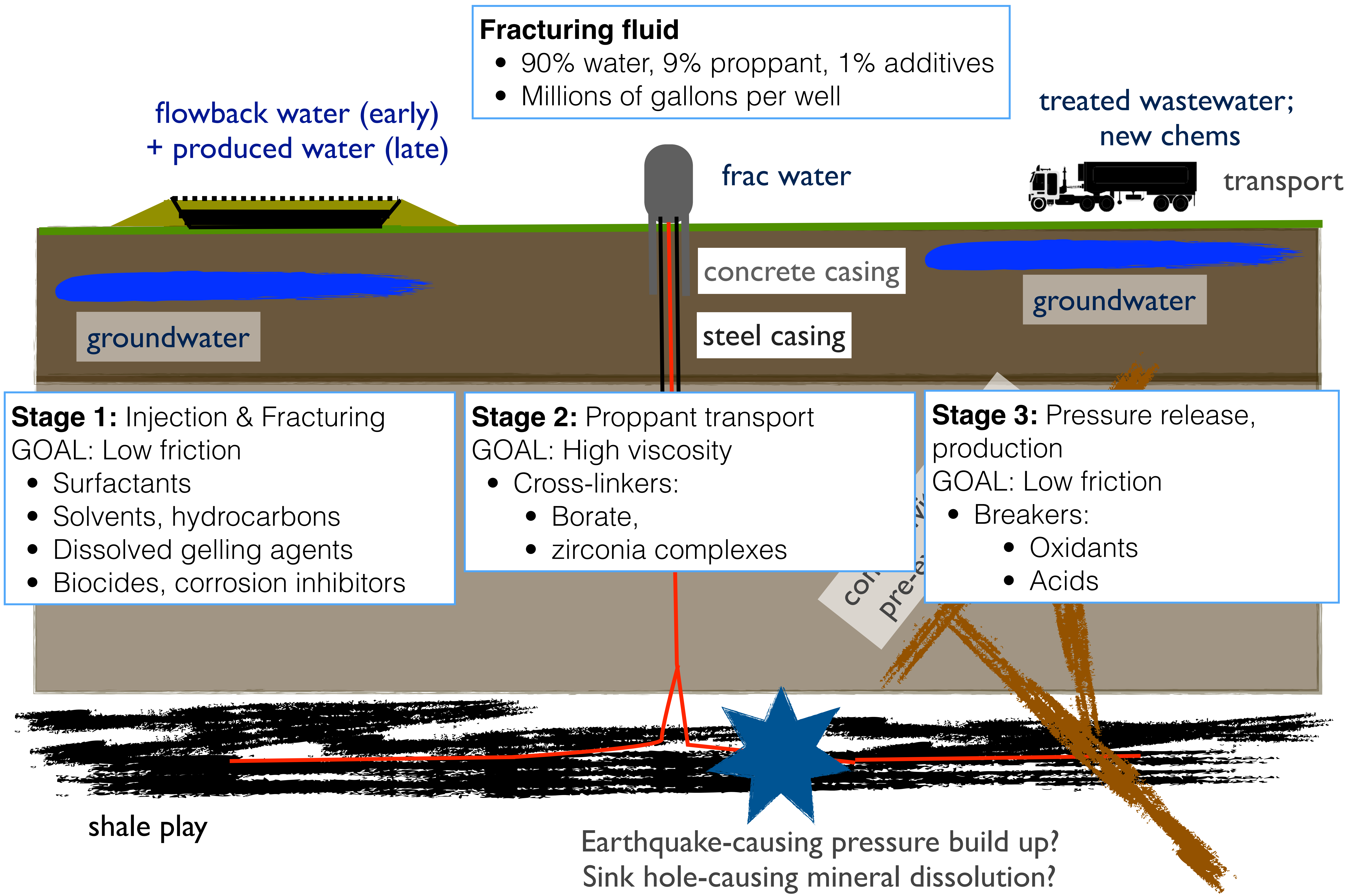
HORIZONTAL DRILLING WITH HYDRAULIC FRACTURING (HDHF)

Natural gas: A vast domestic resource

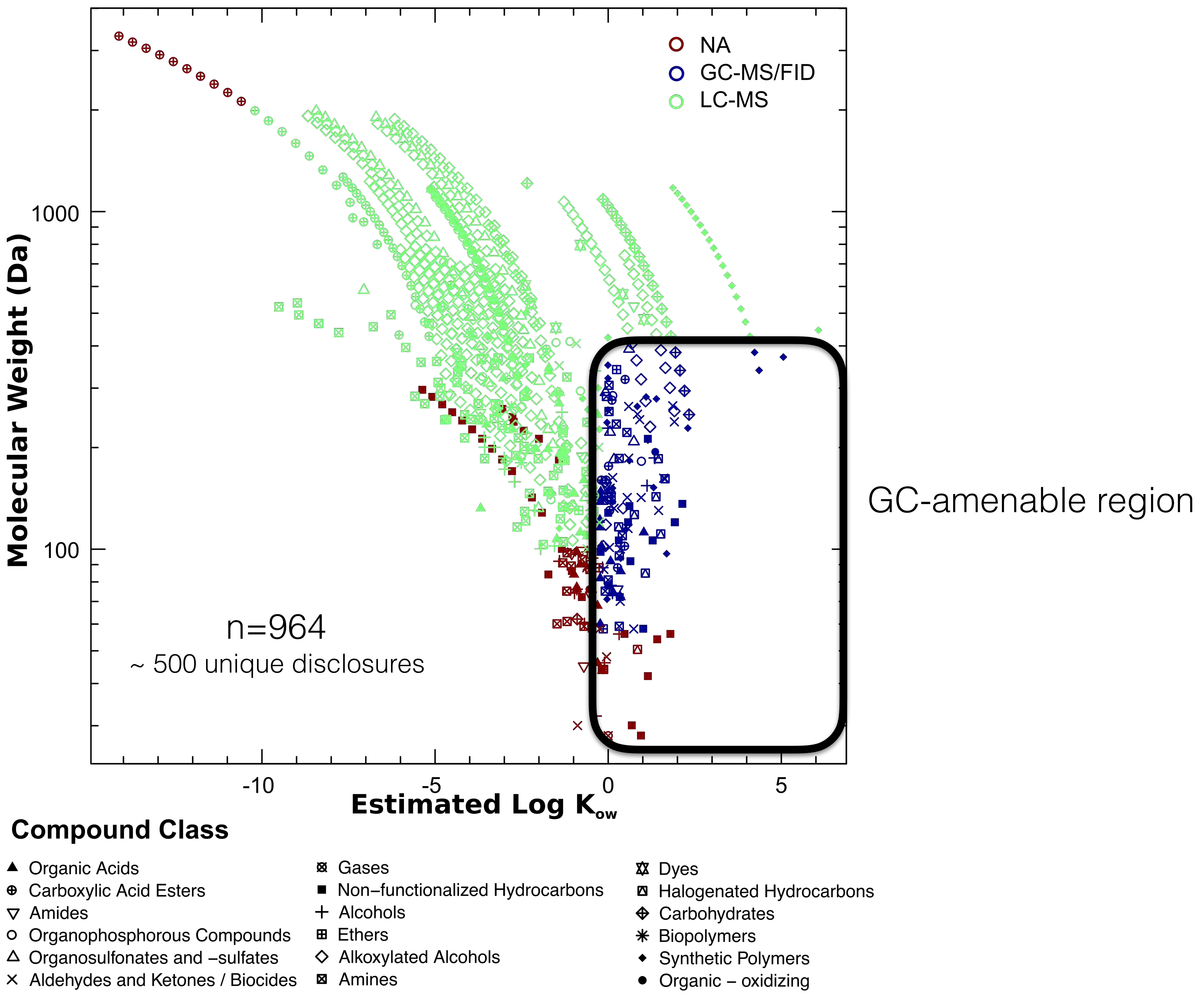
The Eternal Flame, Cook Forest, PA



A remarkable and evolving chemistry



Disclosed components in fracturing fluid

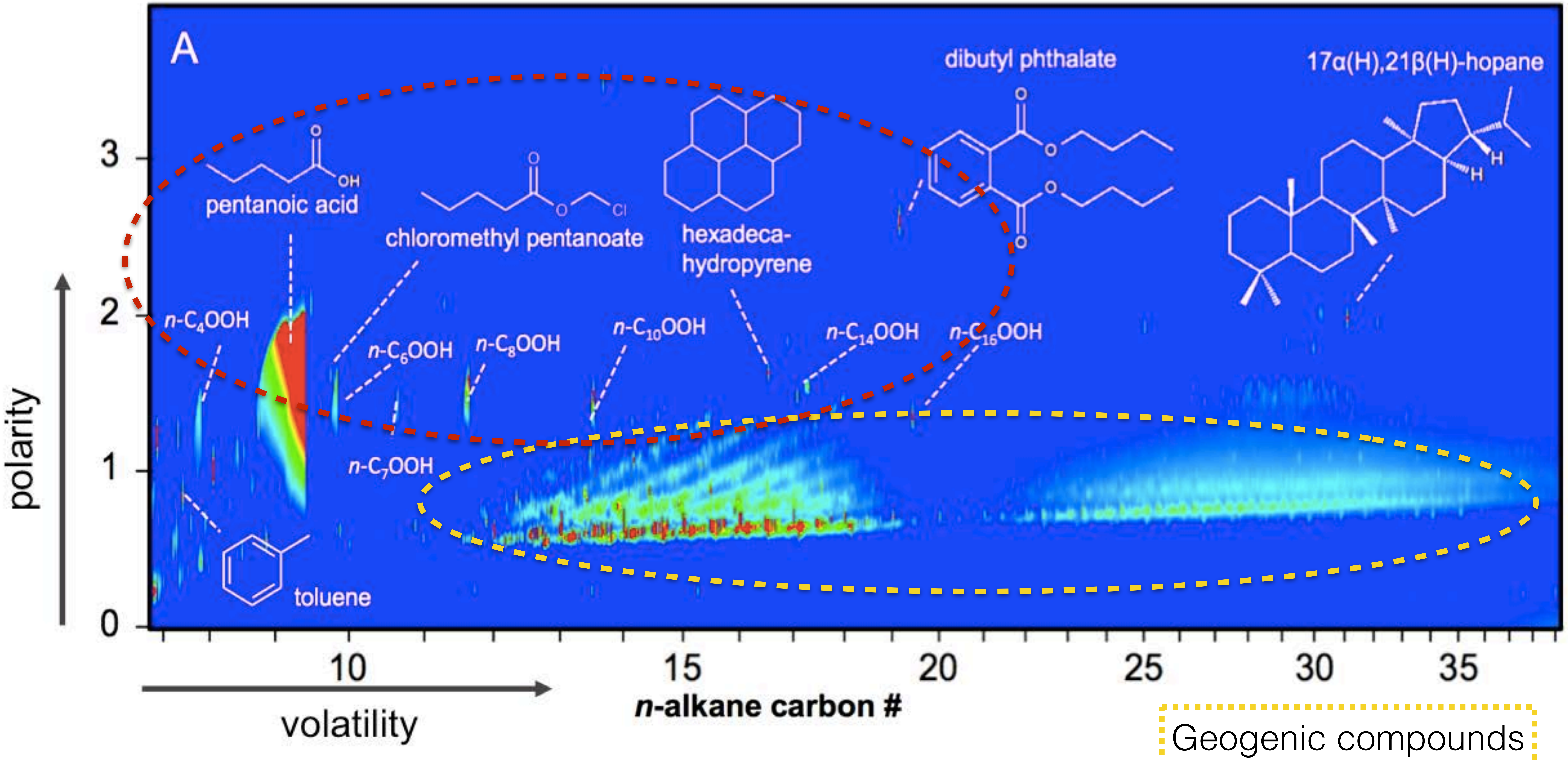


Getzinger, O'Connor, Plata et al. EST 2015

Flowback water: A rich and diverse chemistry (no two wells alike)!

Potentially anthropogenic compounds

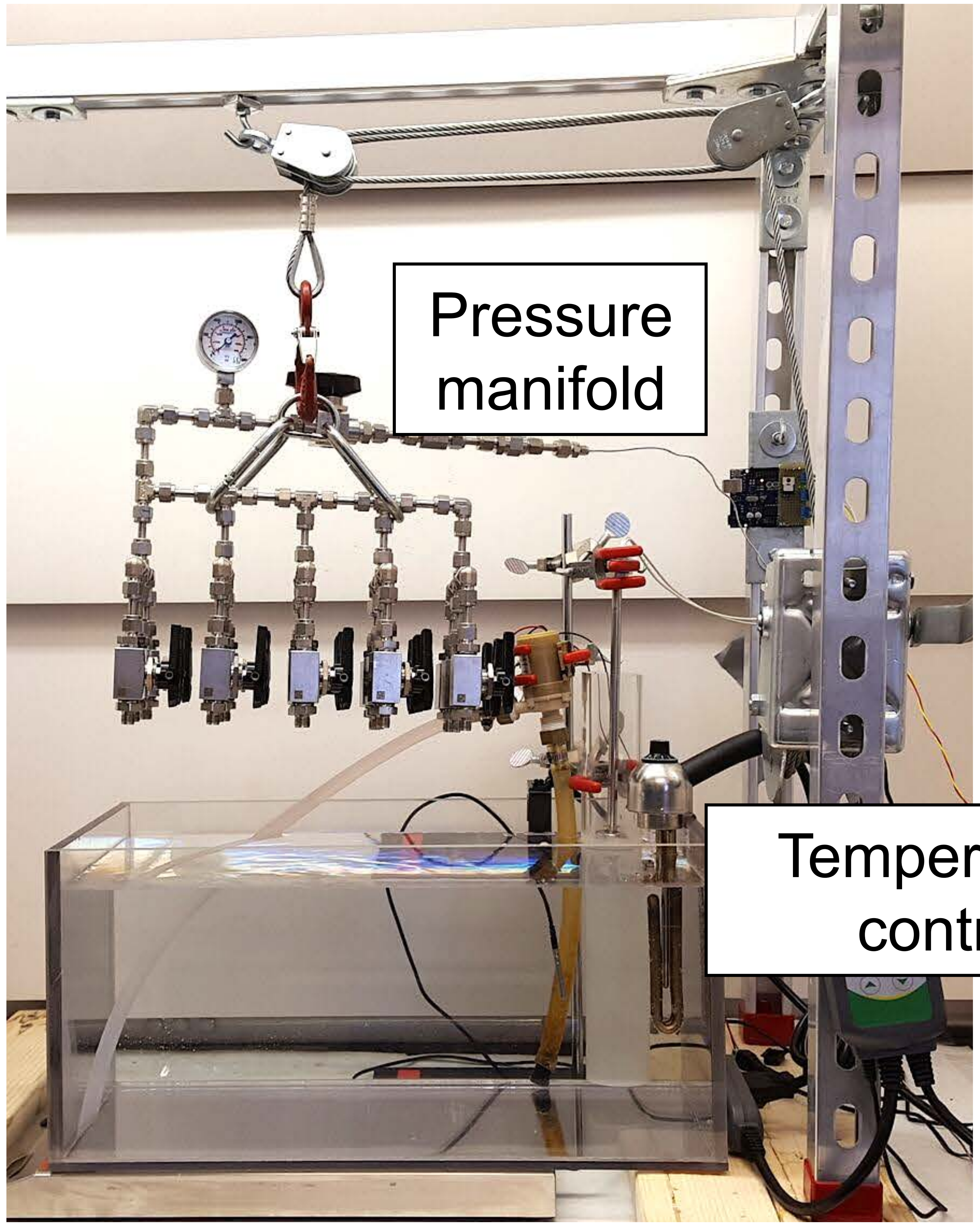
~2,500 detections per sample



Geogenic compounds

Hoelzer, Sumner, Plata et al. EST 2016

Are such transformations possible *in situ*?



3 x 5 reactor vessels

High pressure (5,000 psi)
High temperature (25-95°C)
Throughput, 15
Reproducibility
Residence Time
Price ($), $6k

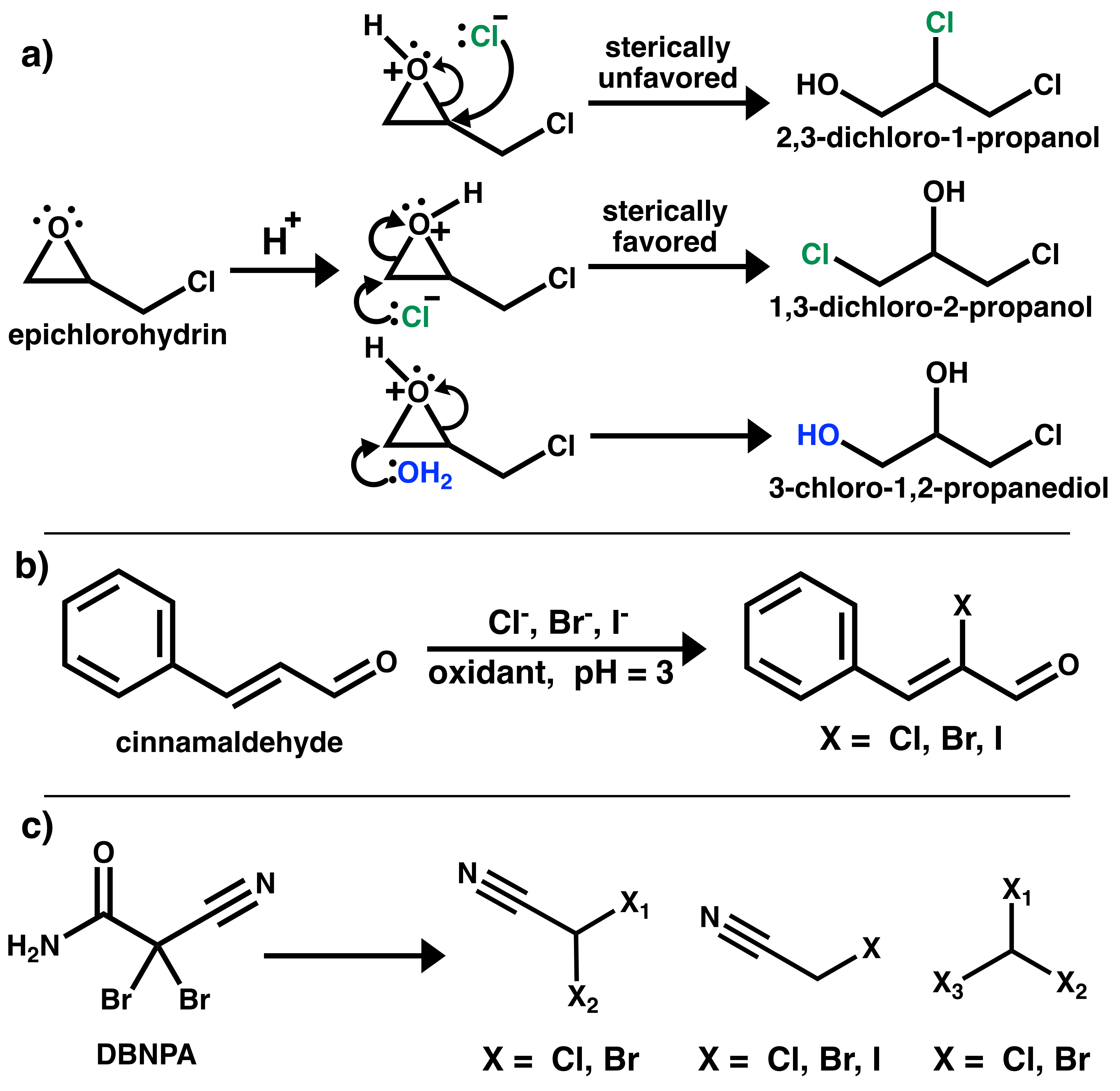
Kinetic Time Series

time points →

triplicate					
	t^1_1	t^2_1	t^3_1	t^4_1	t^5_1
	t^1_2	t^2_2	t^3_2	t^4_2	t^5_2
	t^1_3	t^2_3	t^3_3	t^4_3	t^5_3

Sumner and Plata, *Environ. Sci.: Processes & Impacts (ESPI)*, 2018

Several halogenation reactions occur



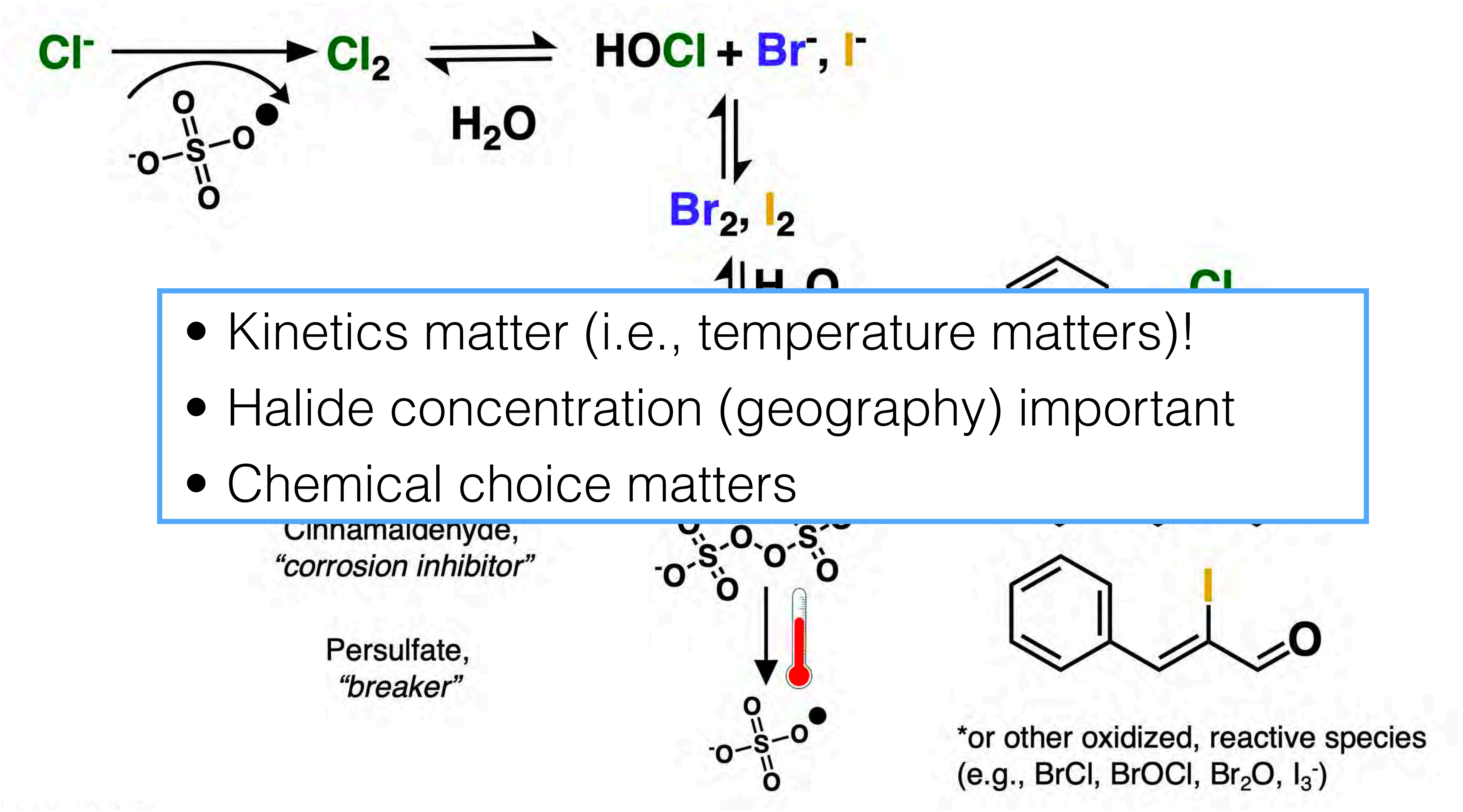
"3-MCPD" (3-monochloro propane diol) formed; expected chemistry

Unexpected halide reactivity

Halomethanes

Sumner and Plata, *EST*, 2018

Geogenic halides can be activated to reactive oxidant species in shale-like conditions



- Kinetics matter (i.e., temperature matters)!
- Halide concentration (geography) important
- Chemical choice matters

Sumner and Plata, EST, 2018

Can we use reaction criteria to *predict* chemical formation?

and…

- Avoid it (operators)
- Test for it (municipality)
- Treat it (wastewater or process engineer)

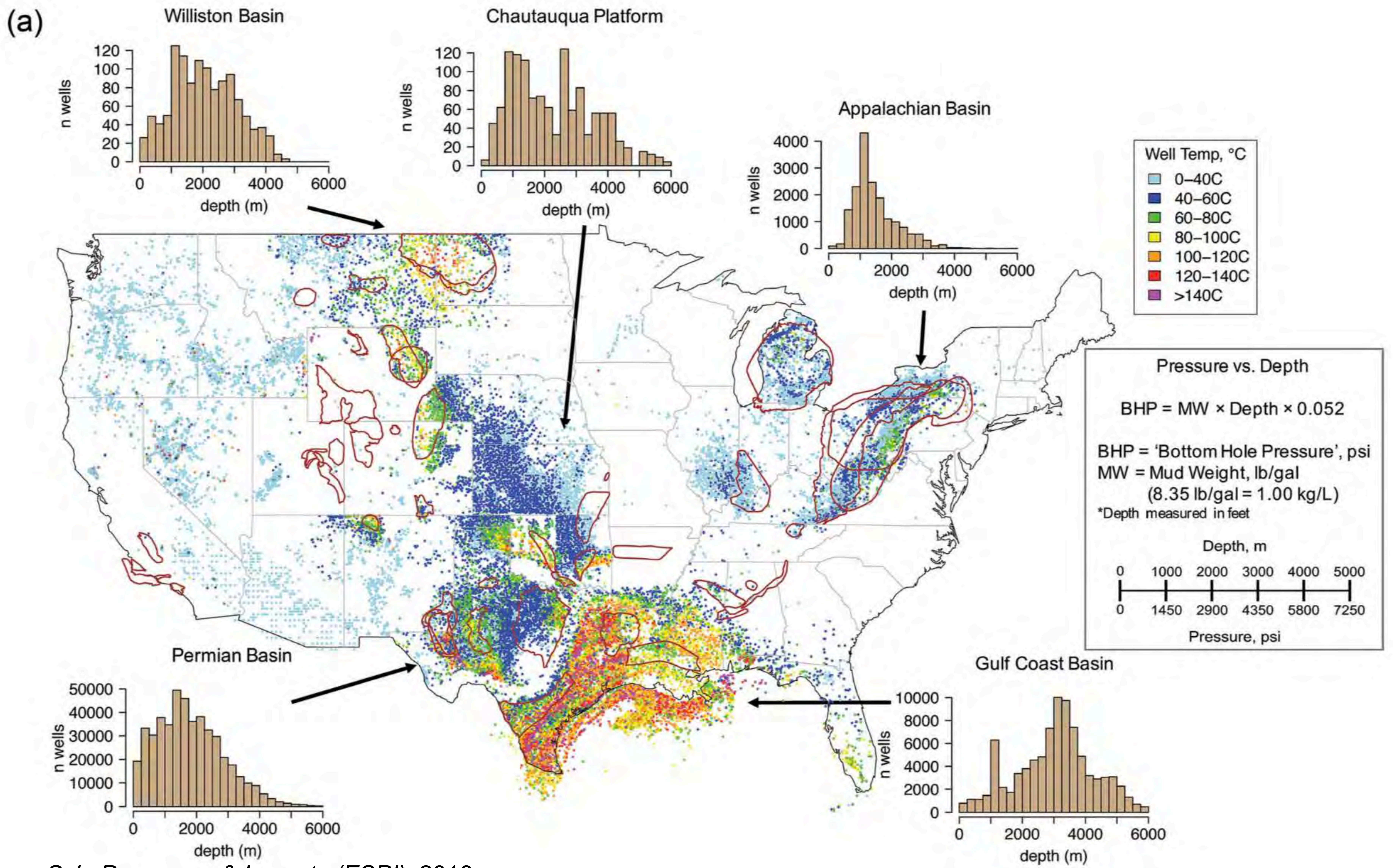
670,000

Number of hydraulic fracturing wells in the US today

238

Number of flowback samples analyzed for chemical constituents

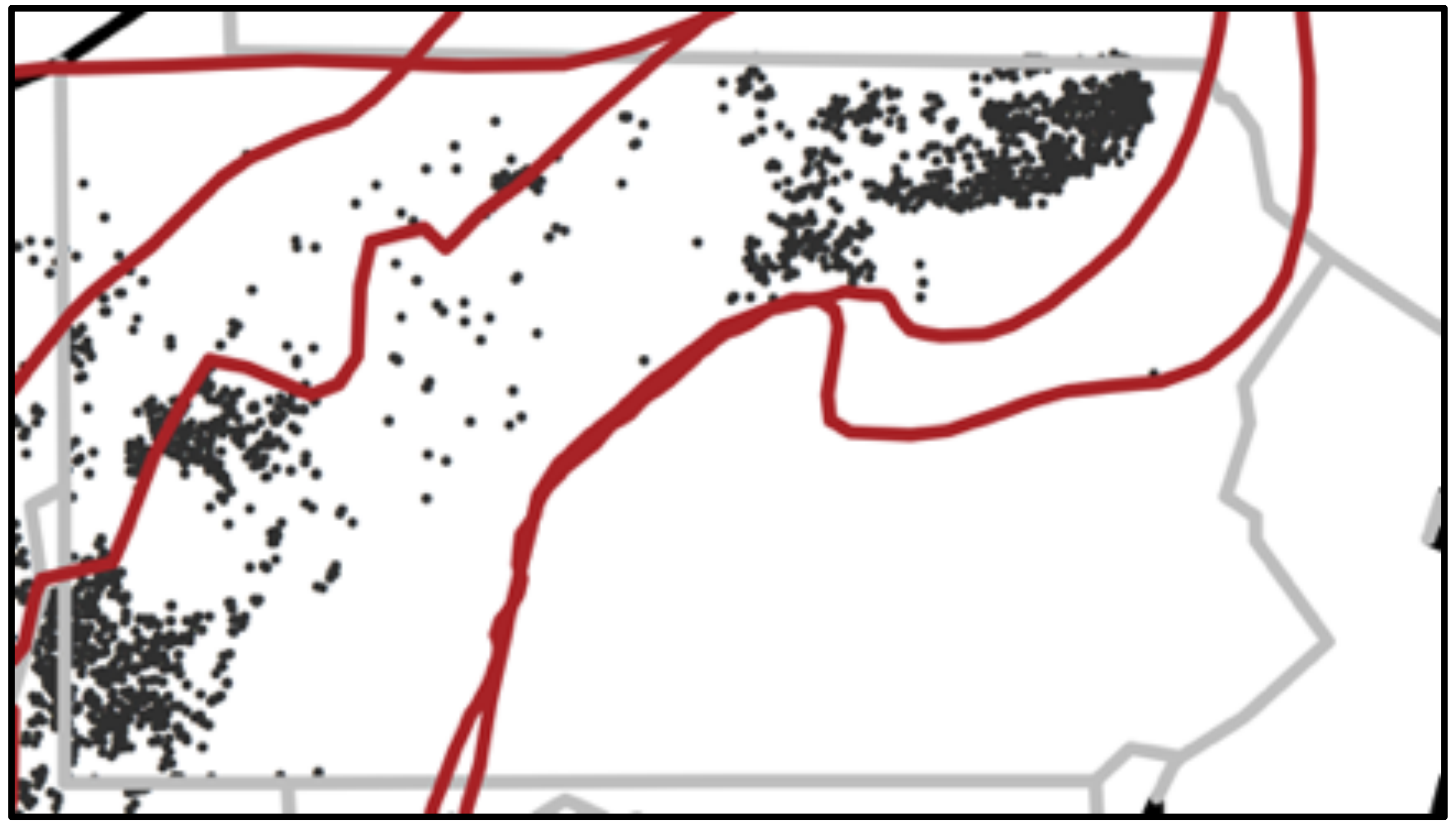
Temperature and pressure (depth); brine composition known with relatively high geospatial specificity



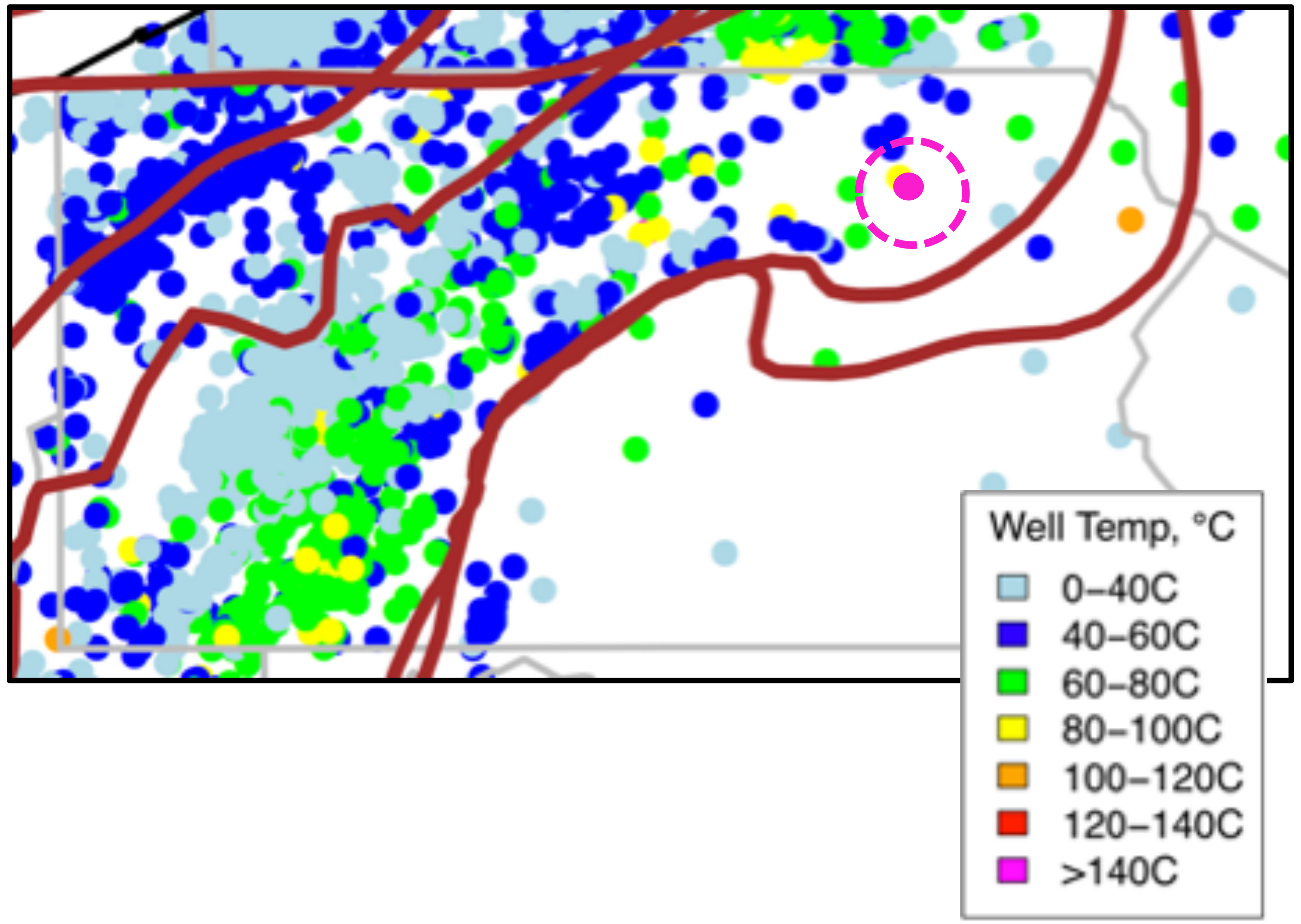
Sumner and Plata, *Environ. Sci.: Processes & Impacts (ESPI)*, 2018

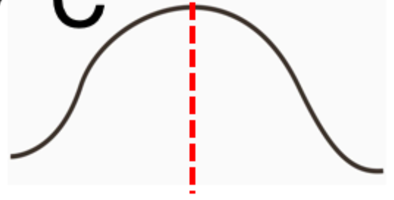
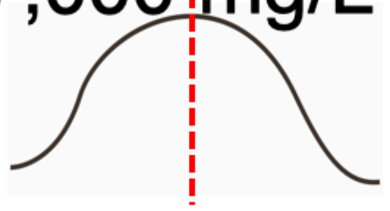
Unify geospatial databases for prediction tools

Disclosure reports



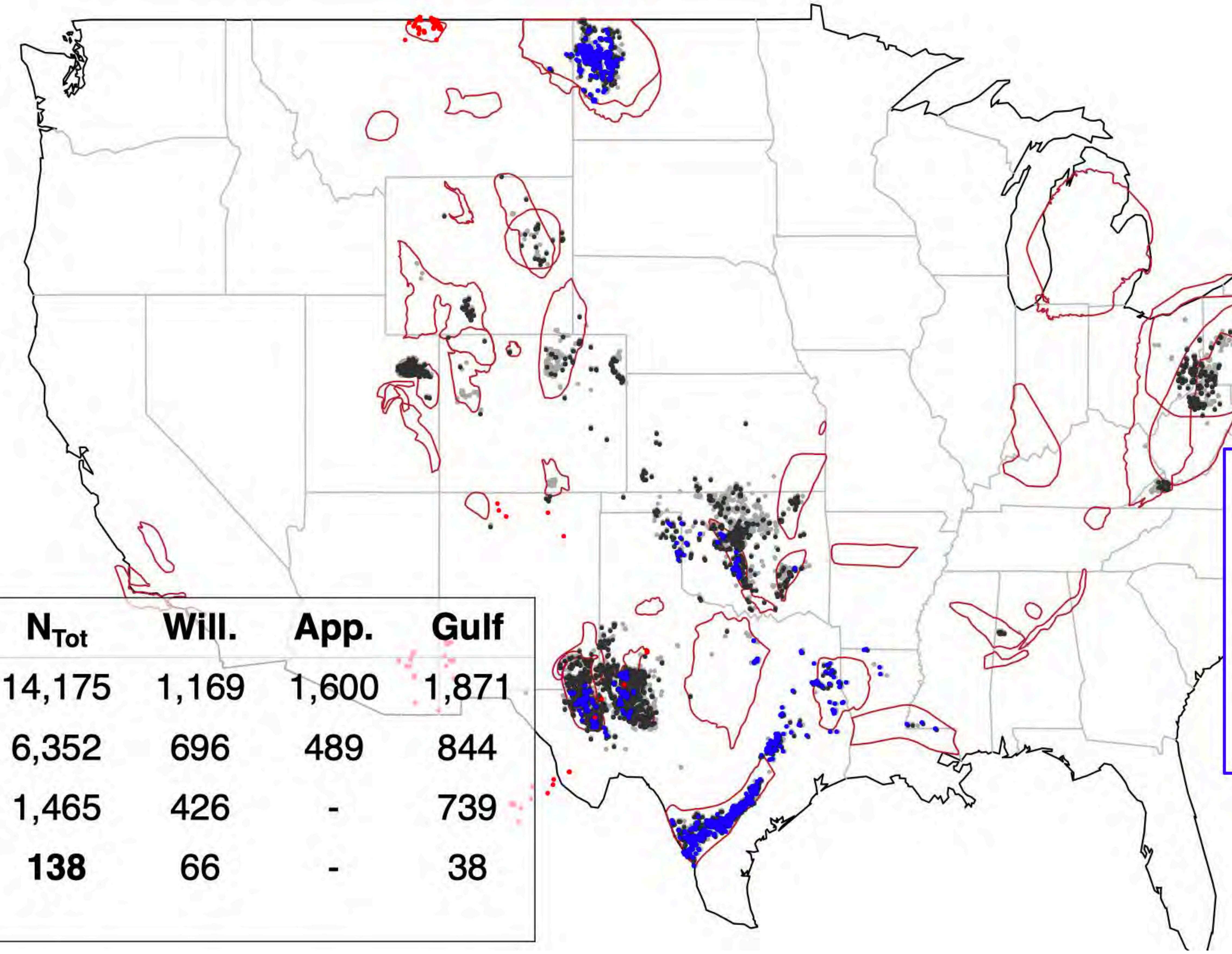
Geochemical conditions



Lat.	Long.	Ingredient	Mass (% w/w)	Temp. (°C)	Cl^- (mg/ L)	pH	DOC	Br^-	I^-
XX	YY	Cinnamaldehyde	conc.	47°C 	37,000 mg/L 				
XX	YY	Persulfate	conc.						

Sumner and Plata; (Defended March 1, 2019…soon to be submitted)!

Mode 1: Prioritize regions of "high risk"



Well Legend	N_{Tot}	Will.	App.	Gulf
cinnamaldehyde	14,175	1,169	1,600	1,871
+ persulfate	6,352	696	489	844
+ well criteria	1,465	426	-	739
+ well criteria + persulfate 75th	**138**	66	-	38

Halogenation Criteria

Temp: 80 °C .
Cl⁻: 50,000 mg L^{-1}
Br⁻: 500 mg L^{-1}

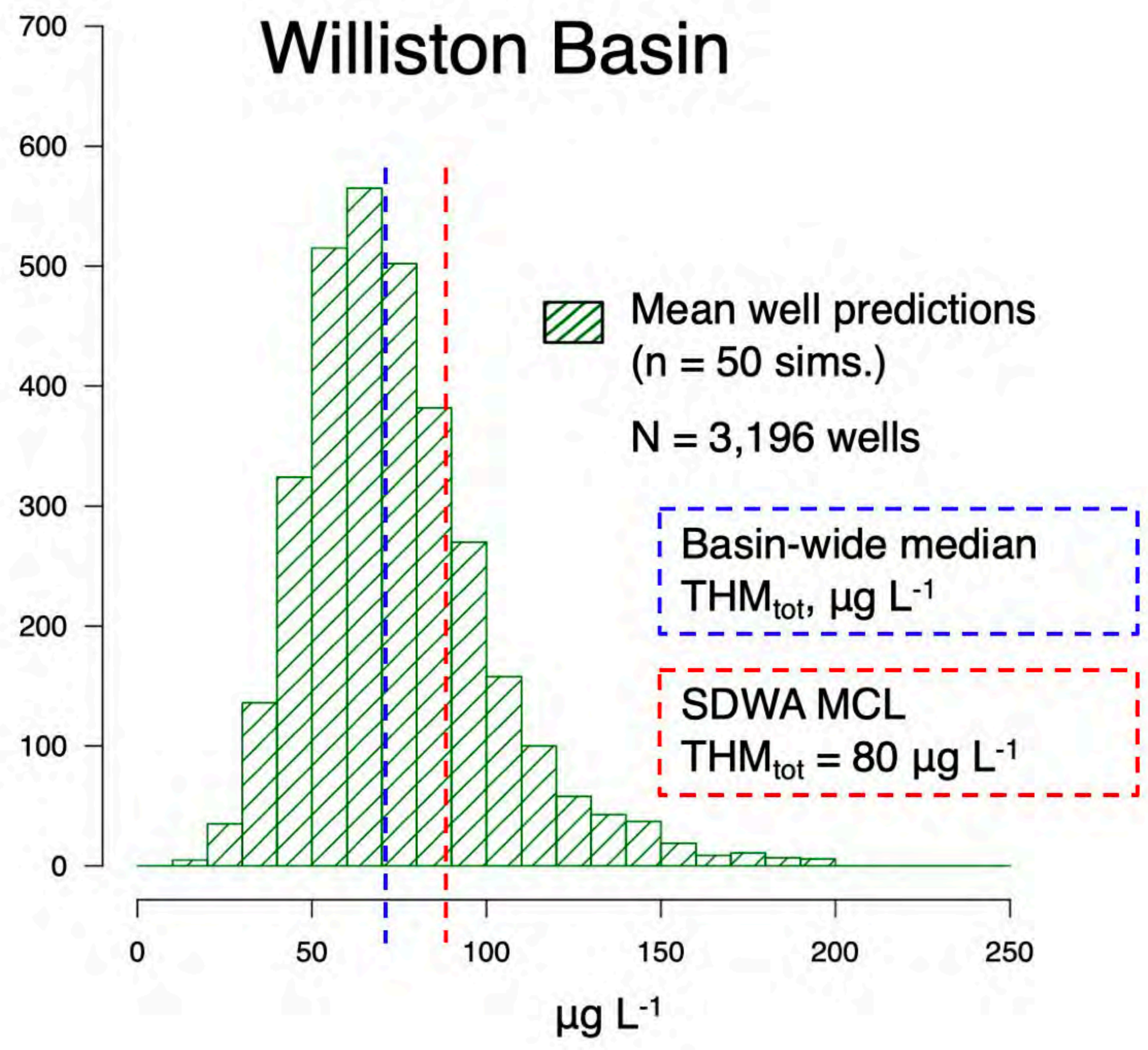
Sumner and Plata; (Defended March 1, 2019…soon to be submitted)!

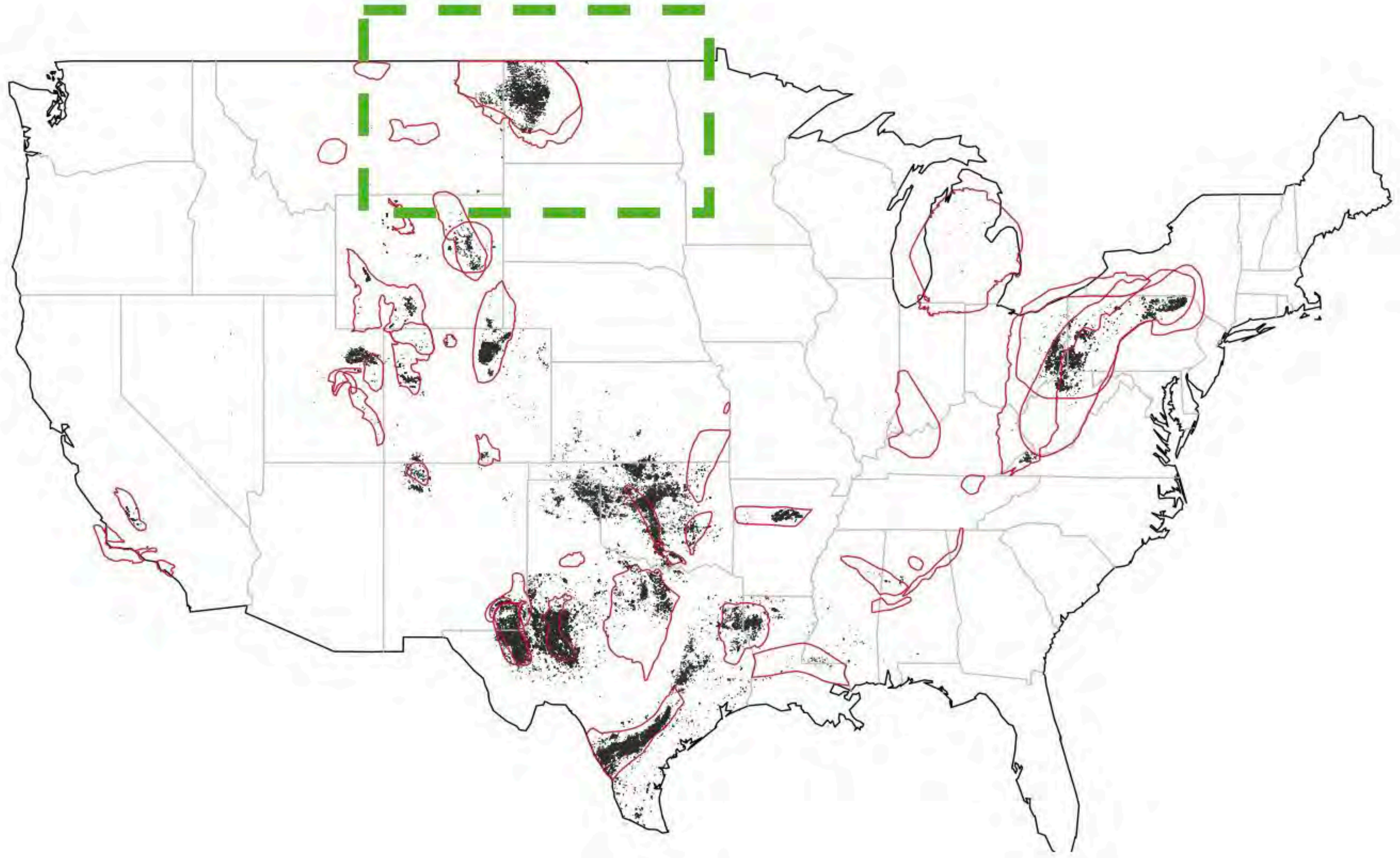
Mode 2: semi-quantitative prediction of reaction byproducts

THM: Trihalomethanes

$$THM_{tot} = 10^{-.375}(t)^{0.258}\left(\frac{Cl_2}{DOC}\right)^{0.194}(pH)^{1.695}(T)^{0.507}([Br^-])^{0.218}$$

Lat.	Long.	Ingredient	Mass (% w/w)	DOC	pH	T	Br^-
XX	YY	Hypochlorite	conc.				
XX	YY	Chlorite	conc.				





Sumner and Plata; unpublished

APPLYING THIS TO THE "PLASTICS" PROBLEM: DESIGNING FOR DEGRADABILITY

Toward high-throughput degradation

Chemical

96/month

- All-glass
- uL polymer
- 2 mL media

LC/MS screen

- ng-pg sensitivity

GCxGC-MS screen

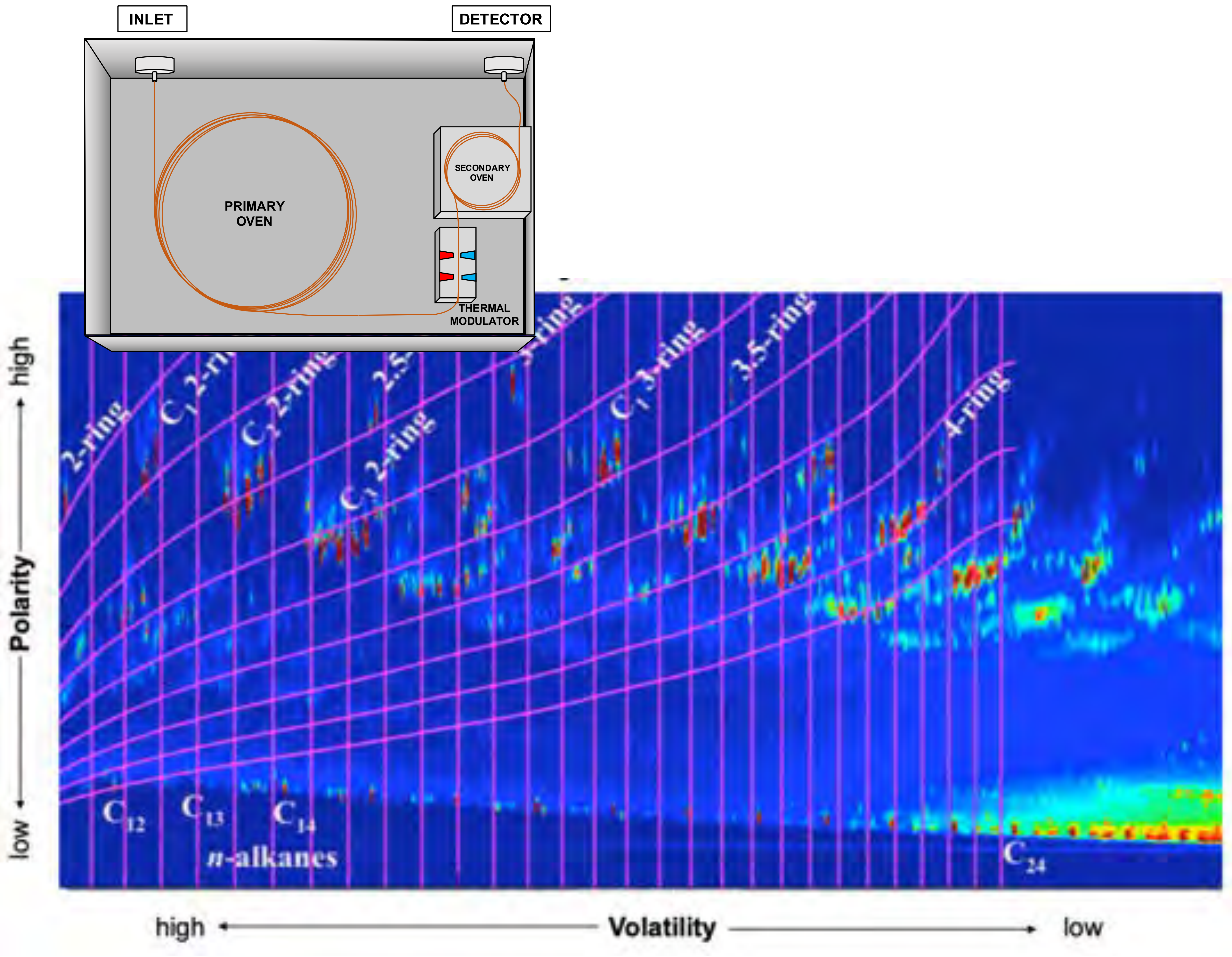
- Physicochemical properties
- Predict toxicity, fate, bioaccumulation

Outcomes:

- Environmental degradation kinetics
- Explicit measure of key environmental indicators

Toward first-principles understanding of degradation kinetics

GCxGC reports on physicochemical properties



log $P_i = aU_{1,i} + bU2_{,i} + c$

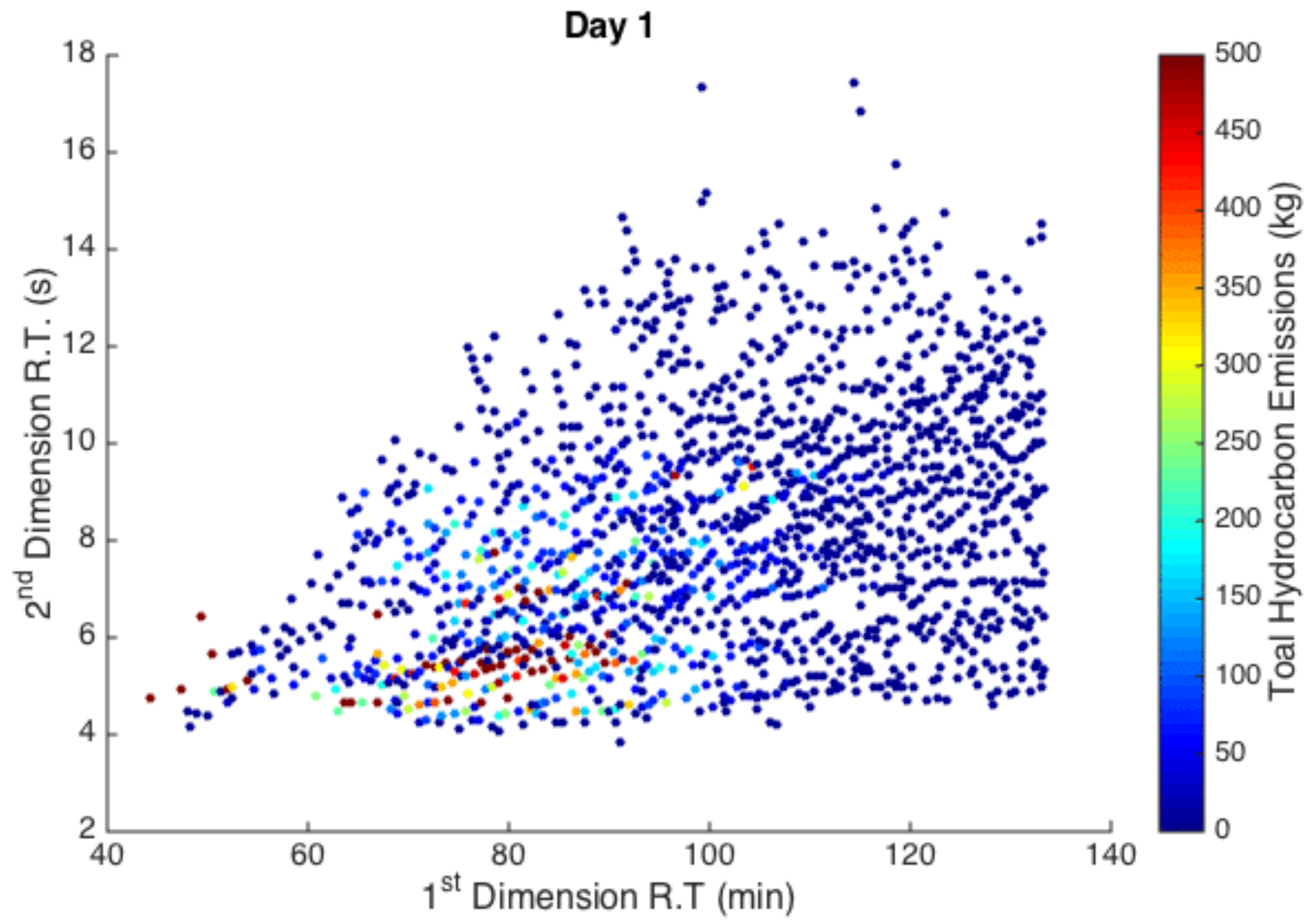
1. Vapor pressure
2. Enthalpy of vaporization
3. Hexadecane-air partition
4. Octanol-air partition
5. Organic carbon-air partition
6. Air-water partition
7. Aqueous solubility
8. Octanol-water partition
9. Organic carbon-water partition
10. Bioconcentration factor
11. Molecular weight

Nabi, Arey, et al. *ES&T 2014*

Arey, J.S. et al. *ES&T 2007*

Arey, J.S.; Plata, D.L.; et al. *ES&T. 2007*

Cute movies



n=1,531
est. 6,000 tons of volatilized material (July);
950-1,050 metric tons SOA formation (July)

Model Parameters

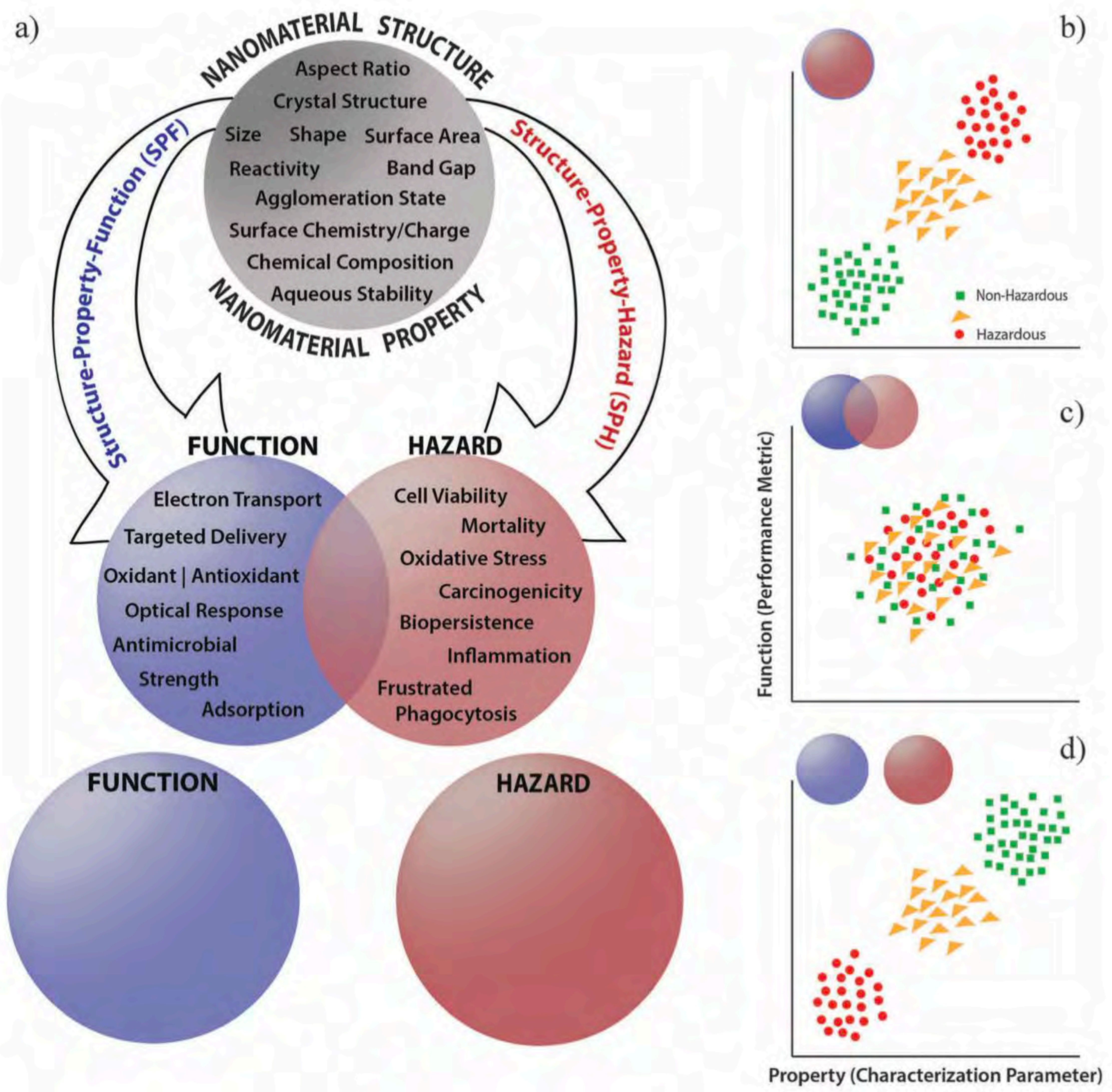
Mean wind speed: 3.34 m s^{-1}
Mean water temp: 9 ^{o}C
Mean depth: 8.5m
Mean particle size: 0.5 um
daily recharge;
sorption equilibrium rapid;
nC$_9$-nC$_{25}$ range

Dompierre and Barbour (2016)

Nota bona: Emissions shown for Athabasca oil sands process water

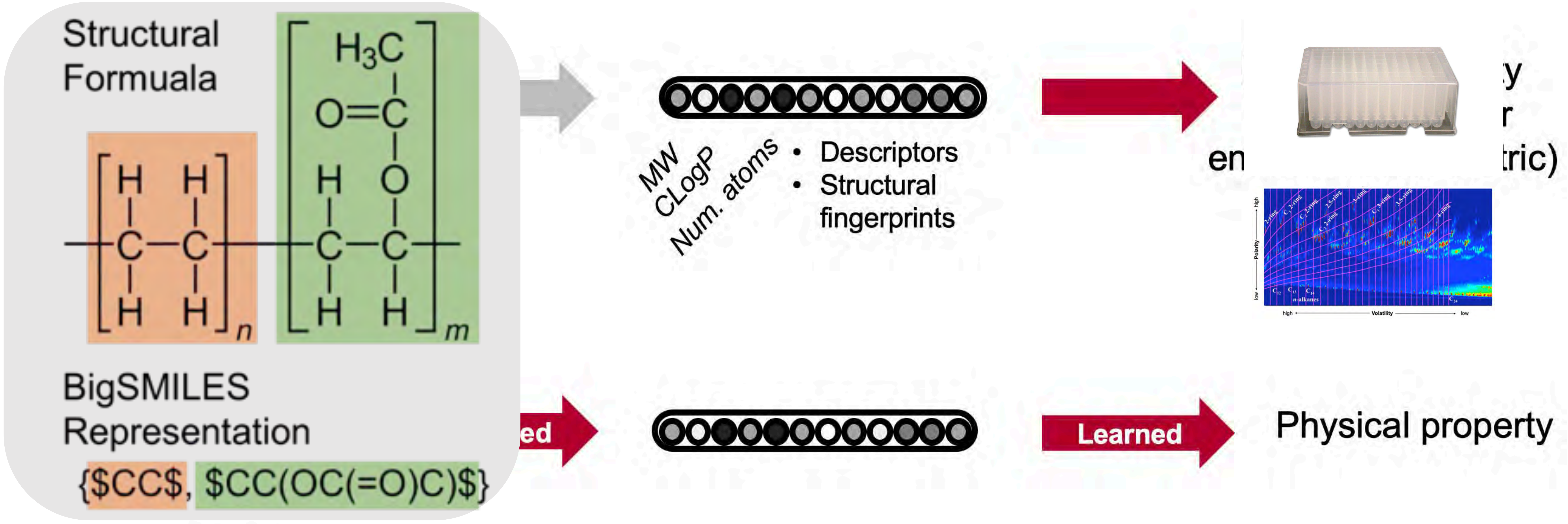
Drollette, Plata; unpublished
after Liggio, Plata et al. Nature 2016

How does the fundamental chemical structure inform the material and environmental performance?

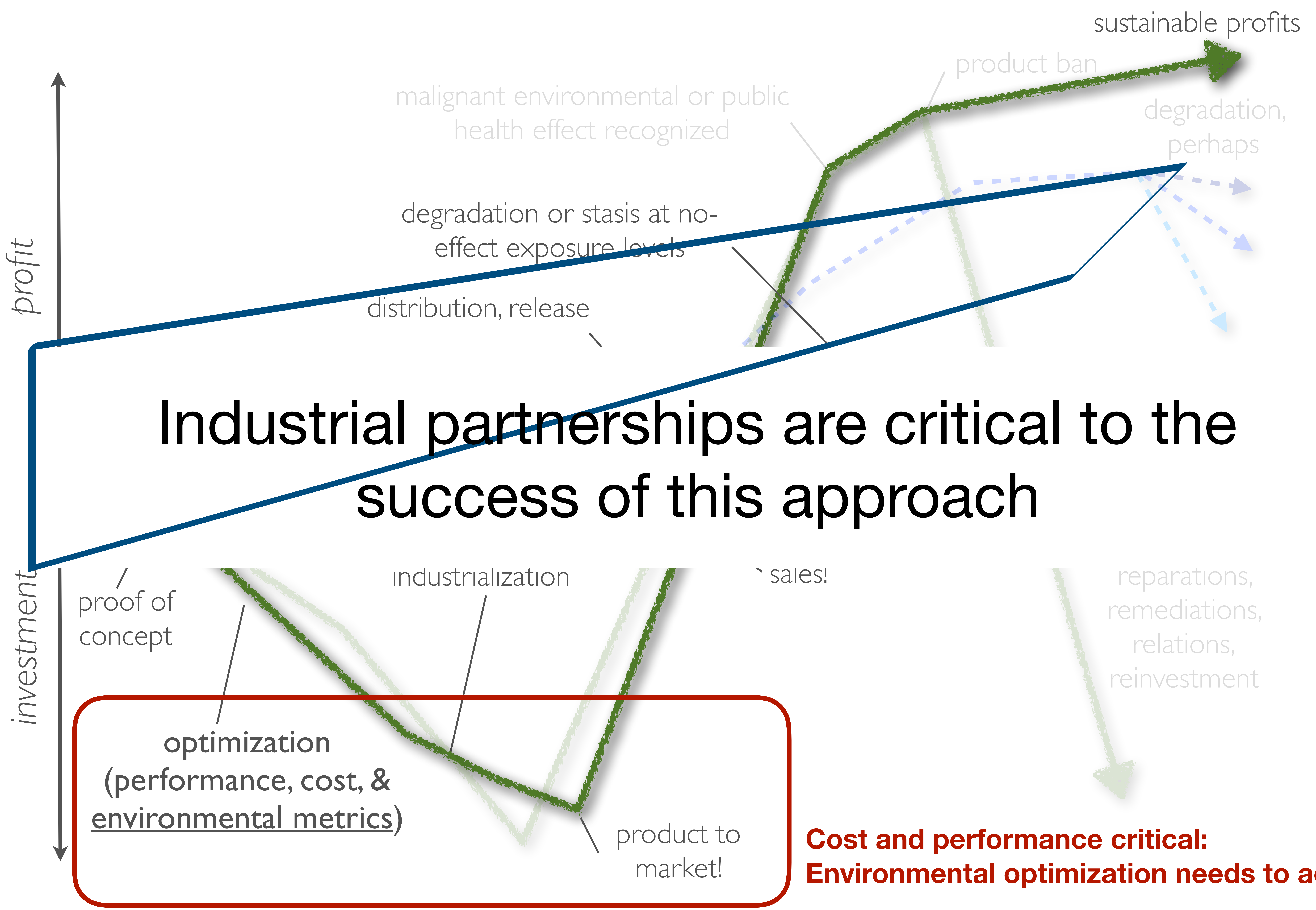


Gilbertson, Plata et al. *Chem Soc. Rev.*, 2015

Long-term vision: *a priori* prediction of environmental *and* material performance



T.S. Lin, C. Cowley, **K.F. Jensen, B.D. Olsen**. ACS Central Science 2019
C.W. Coley, **R. Barzilay**, W.H. Green, **T.S. Jaakkola, and KF. Jensen**, “Convolutional Embedding of Attributed Molecular Graphs for Physical Property Prediction,” J. Chem. Inf. Model., 57 (8), 1757–1772 (2017).

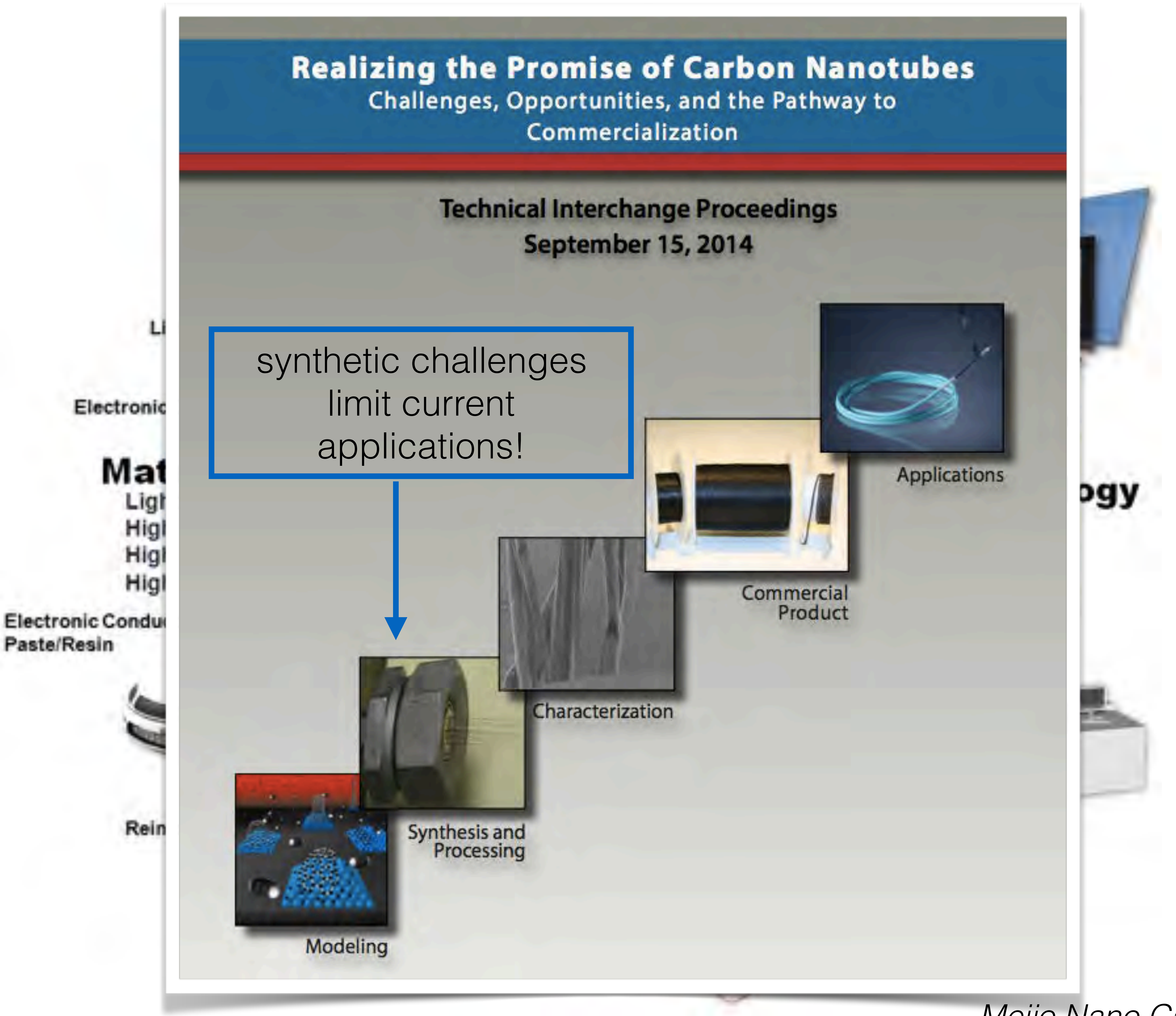


Industrial partnerships are critical to the success of this approach

Cost and performance critical:
Environmental optimization needs to add value

Thank you attendees!

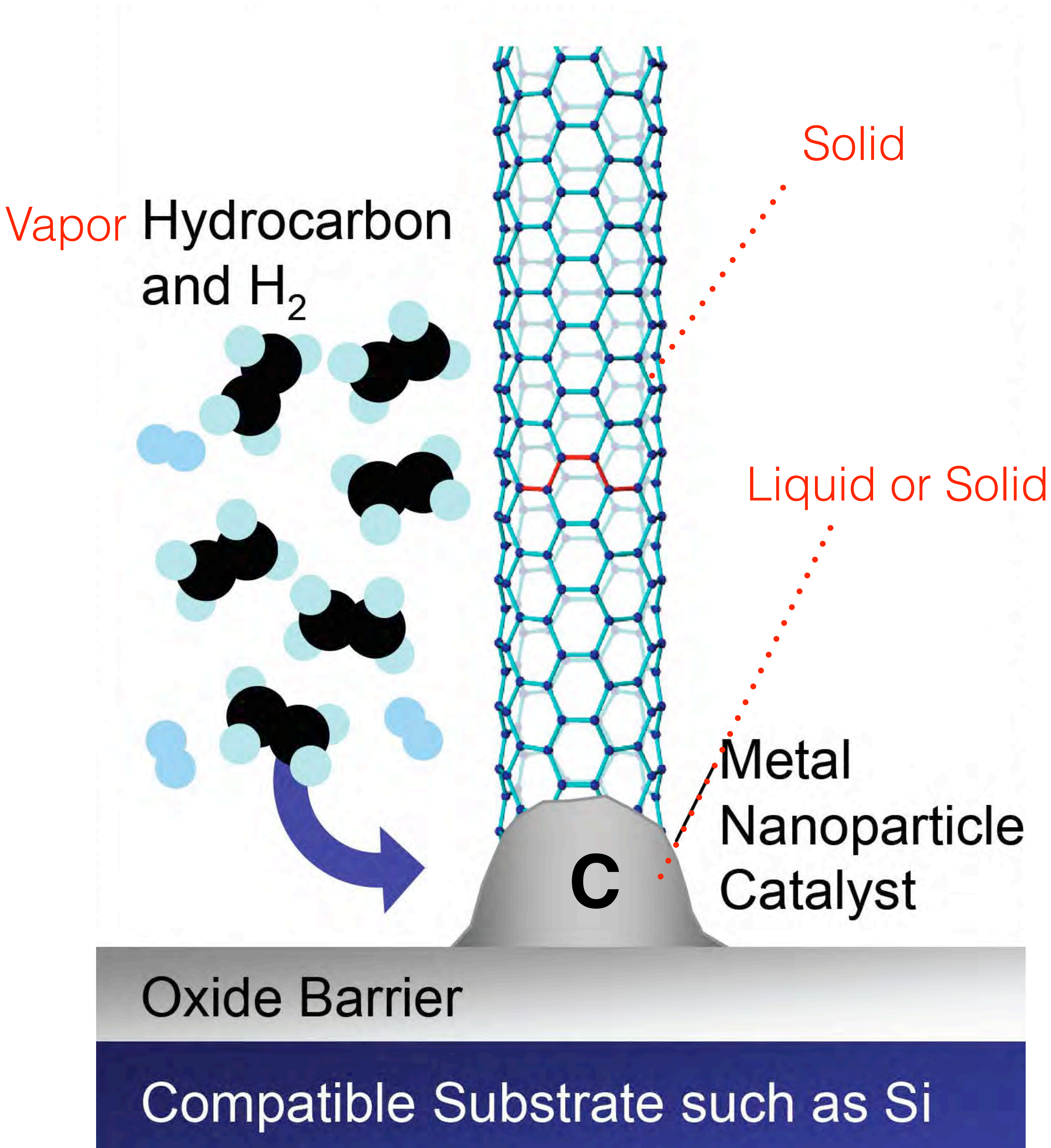
Applications of graphene and CNTs

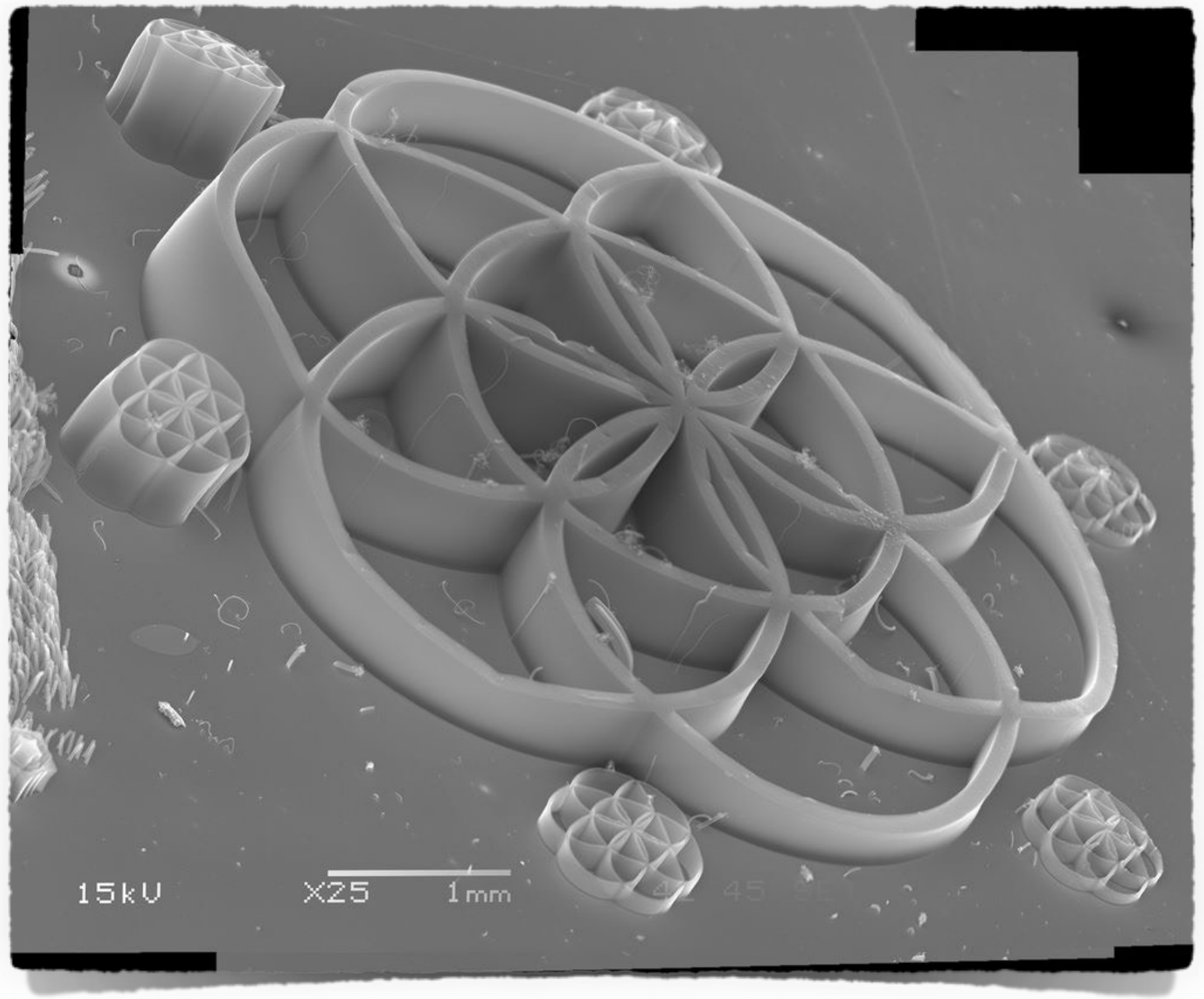


Meijo Nano Carbon Corp Ltd.

Proposed mechanism of nanotube growth

Vapor-Liquid-Solid (VLS) or Vapor-Solid-Solid (VSS) Model

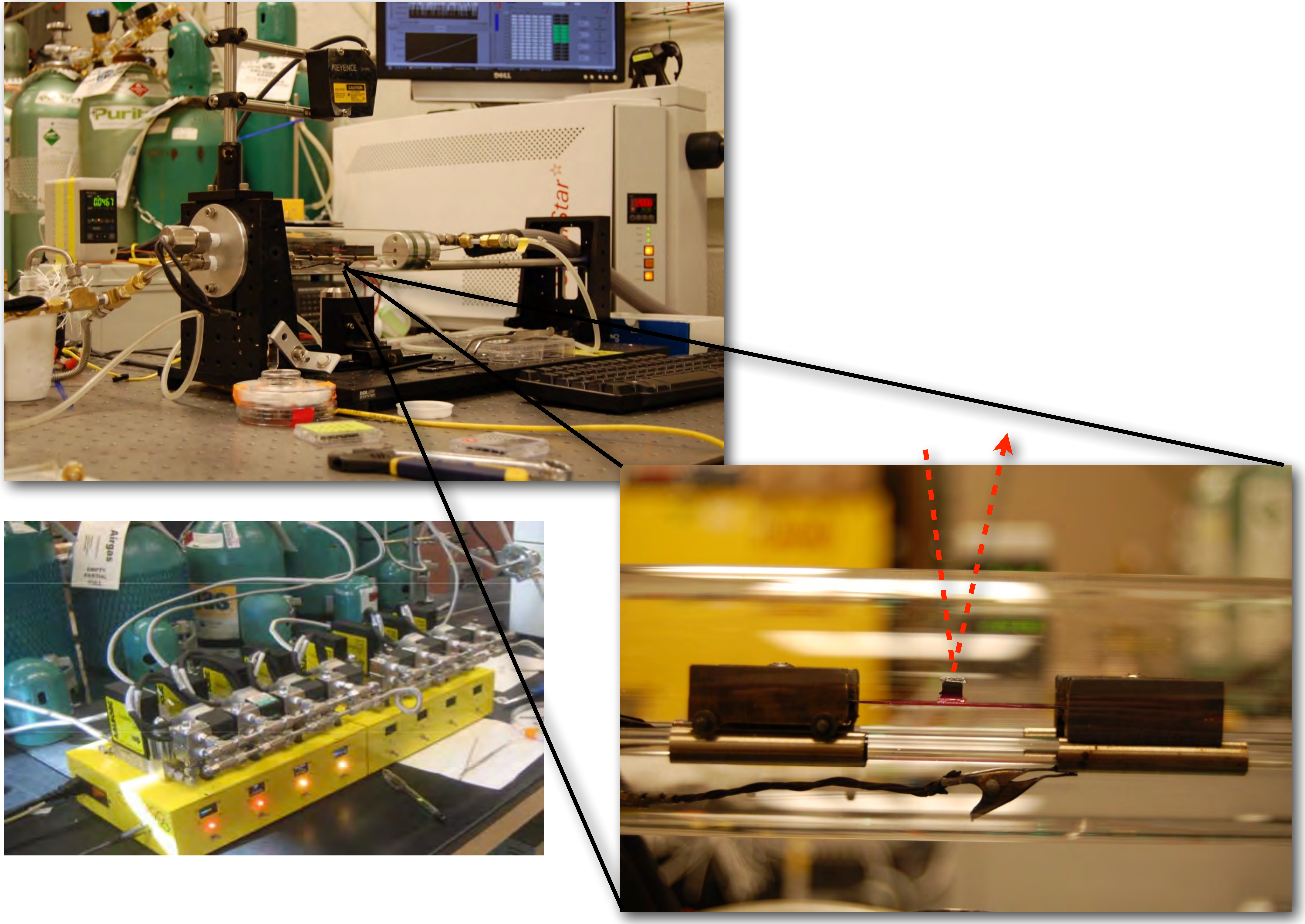




nanobliss.com; A. John Hart MIT 2006

Baker Carbon 1989

A chemist's route to a mechanism: Kinetics!



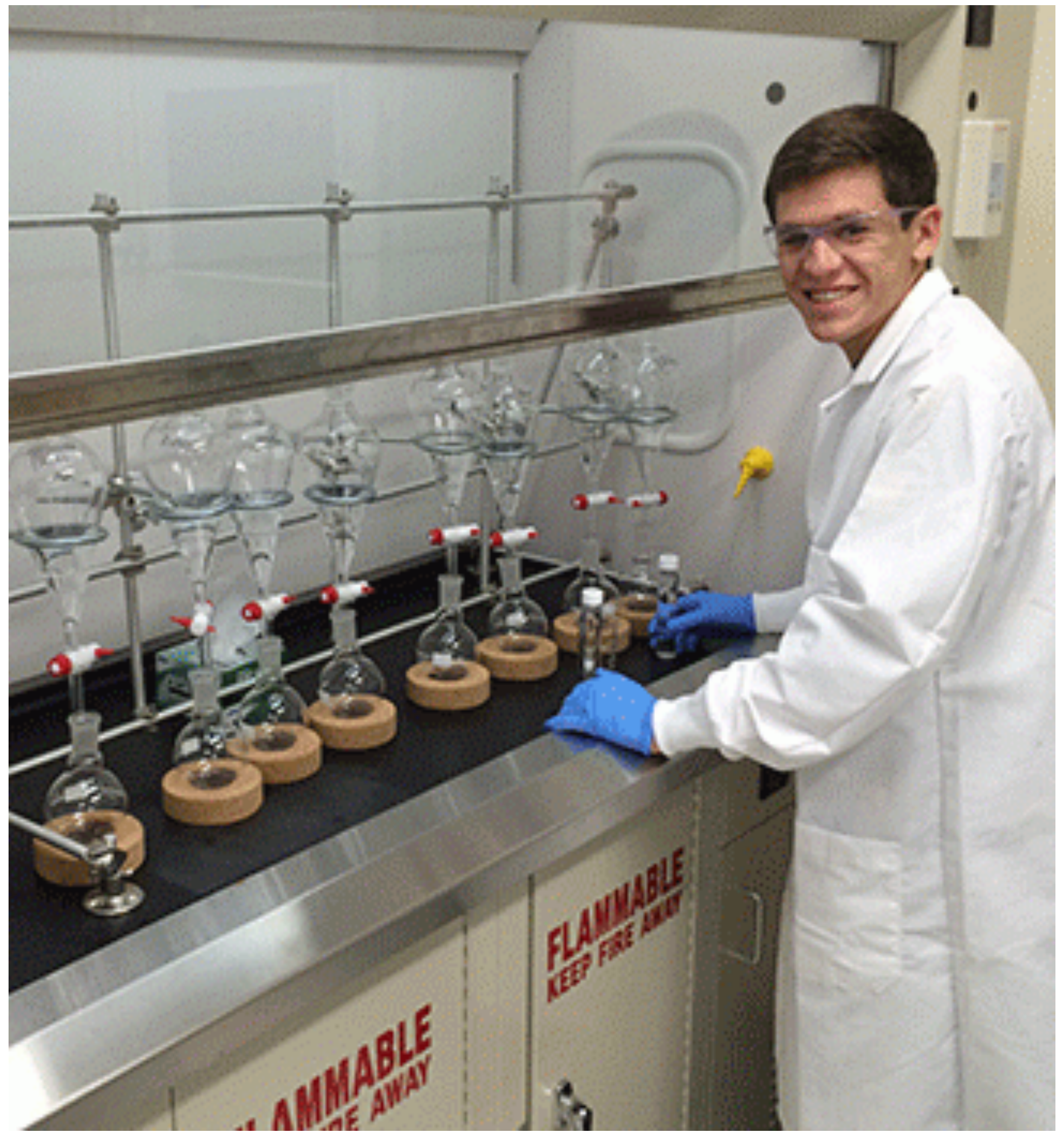
In collaboration with:
John Hart (MechE, MIT)
Brian Wardle (AeroAstro, MIT)

Nanotechnology

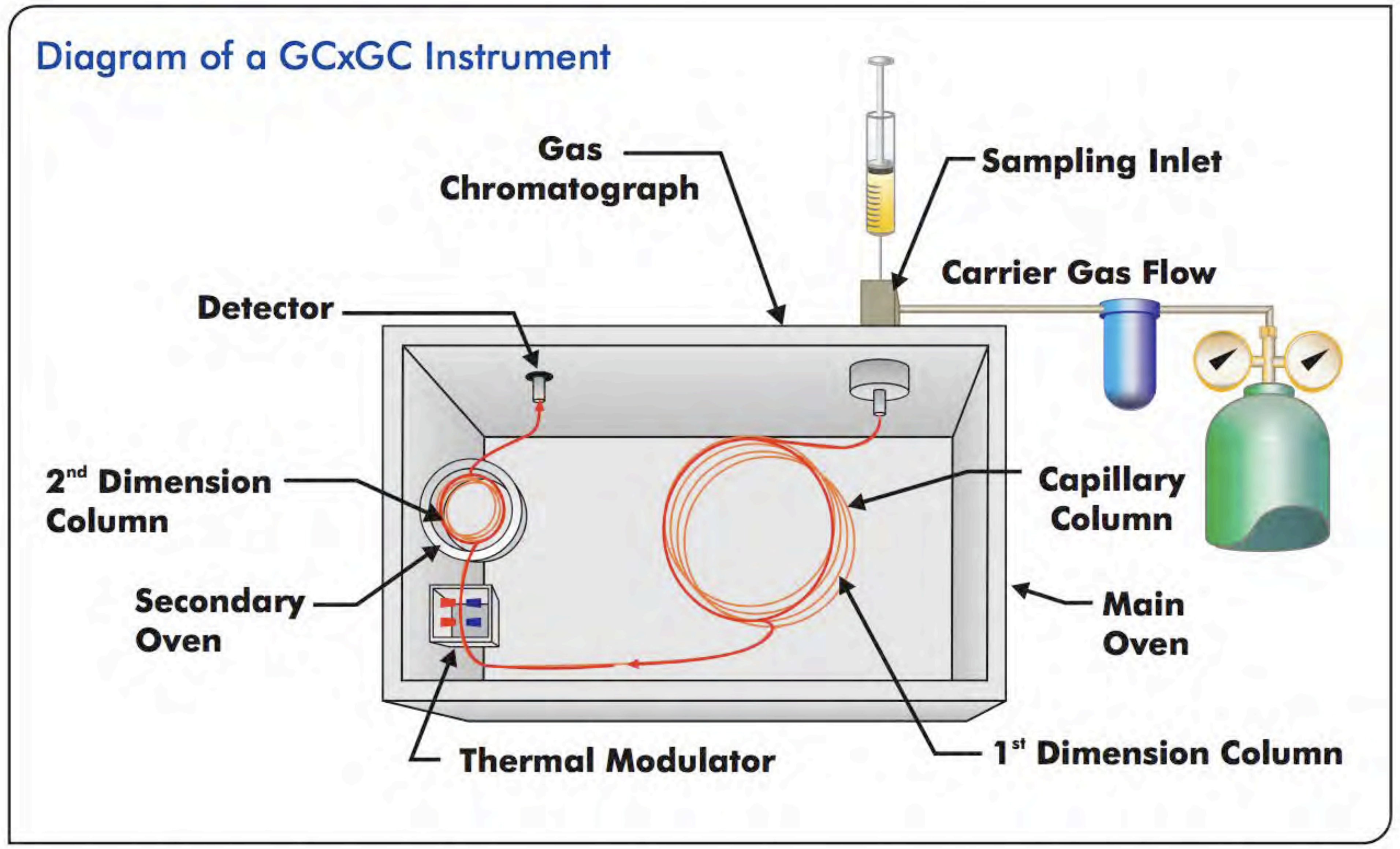
\ˌna-nō-tek-ˈnä-lə-jē\:

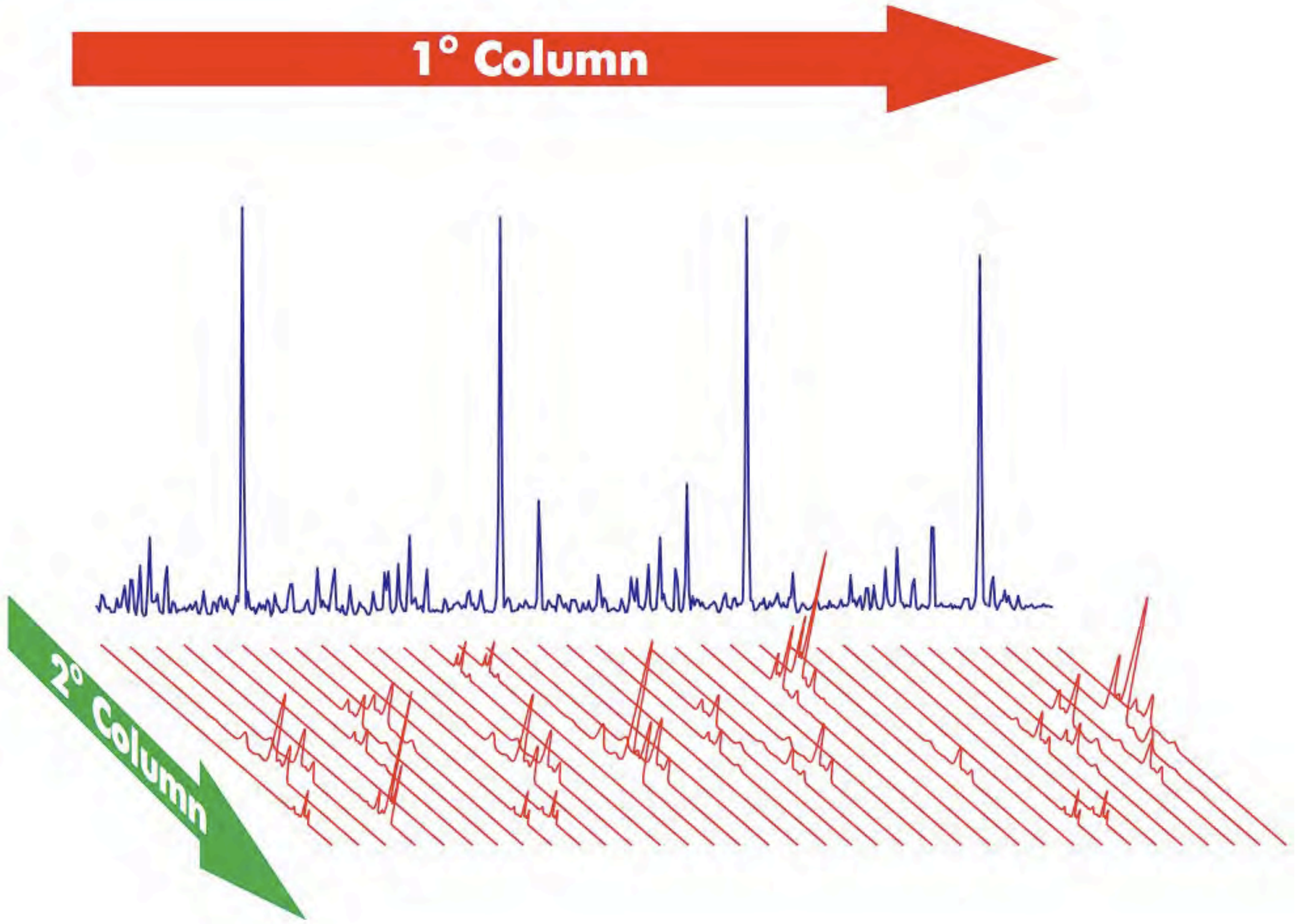
the branch of technology that deals with dimensions and tolerances of less than 100 nanometers, especially the manipulation of individual atoms and molecules

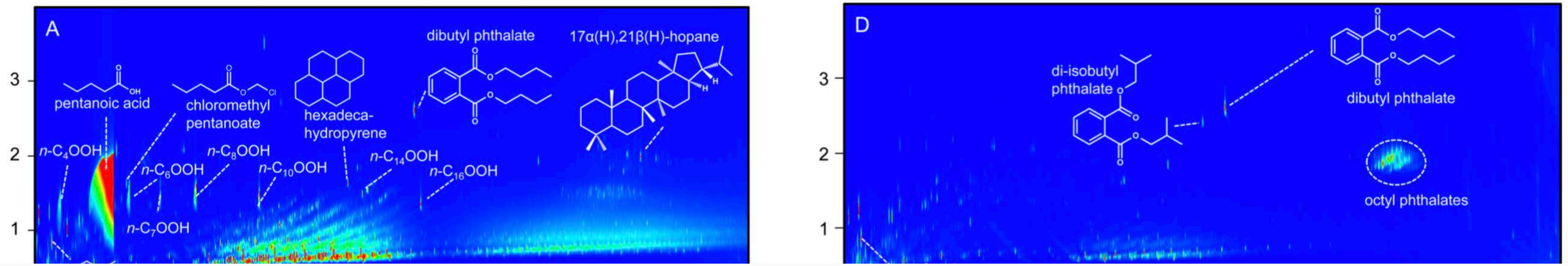
Extract and enrich via liquid-liquid extraction



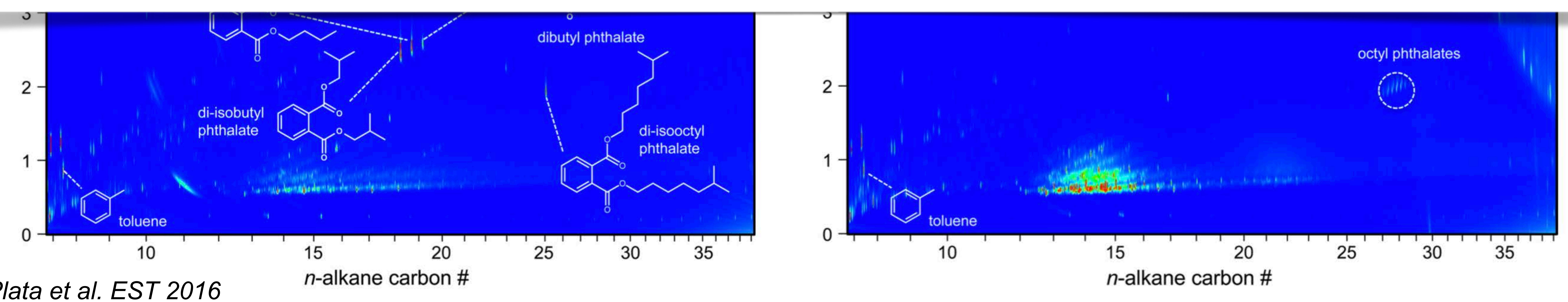
Better separation enable process studies in complex mixtures: GCxGC





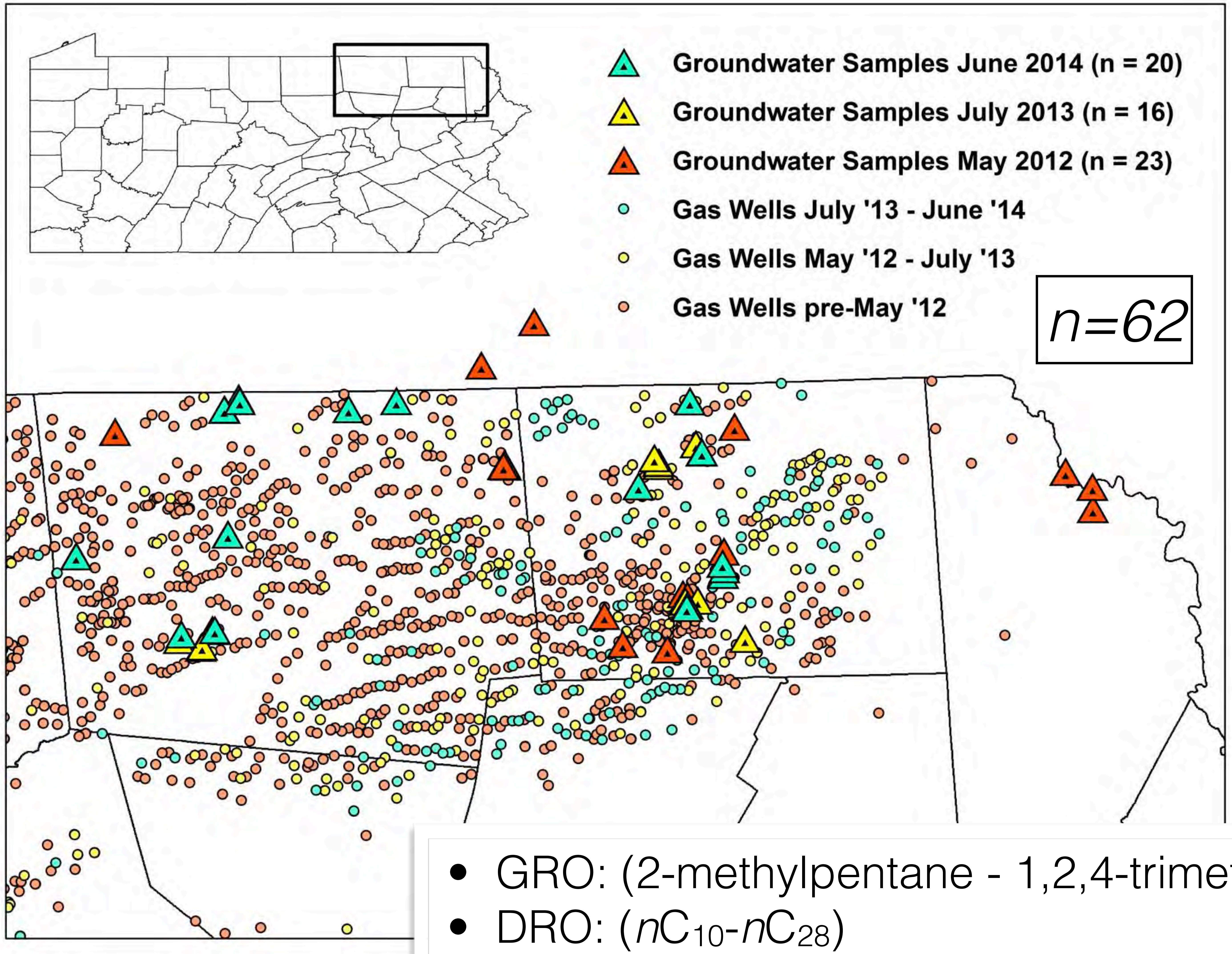


- Hopane biomarkers as fingerprints of formation source, thermal history
- Unique fatty acid distribution
- Phthalates stand out from typical oil hydrocarbons
- Radical initiators detected
- Halogenated compounds mostly as reaction by-products



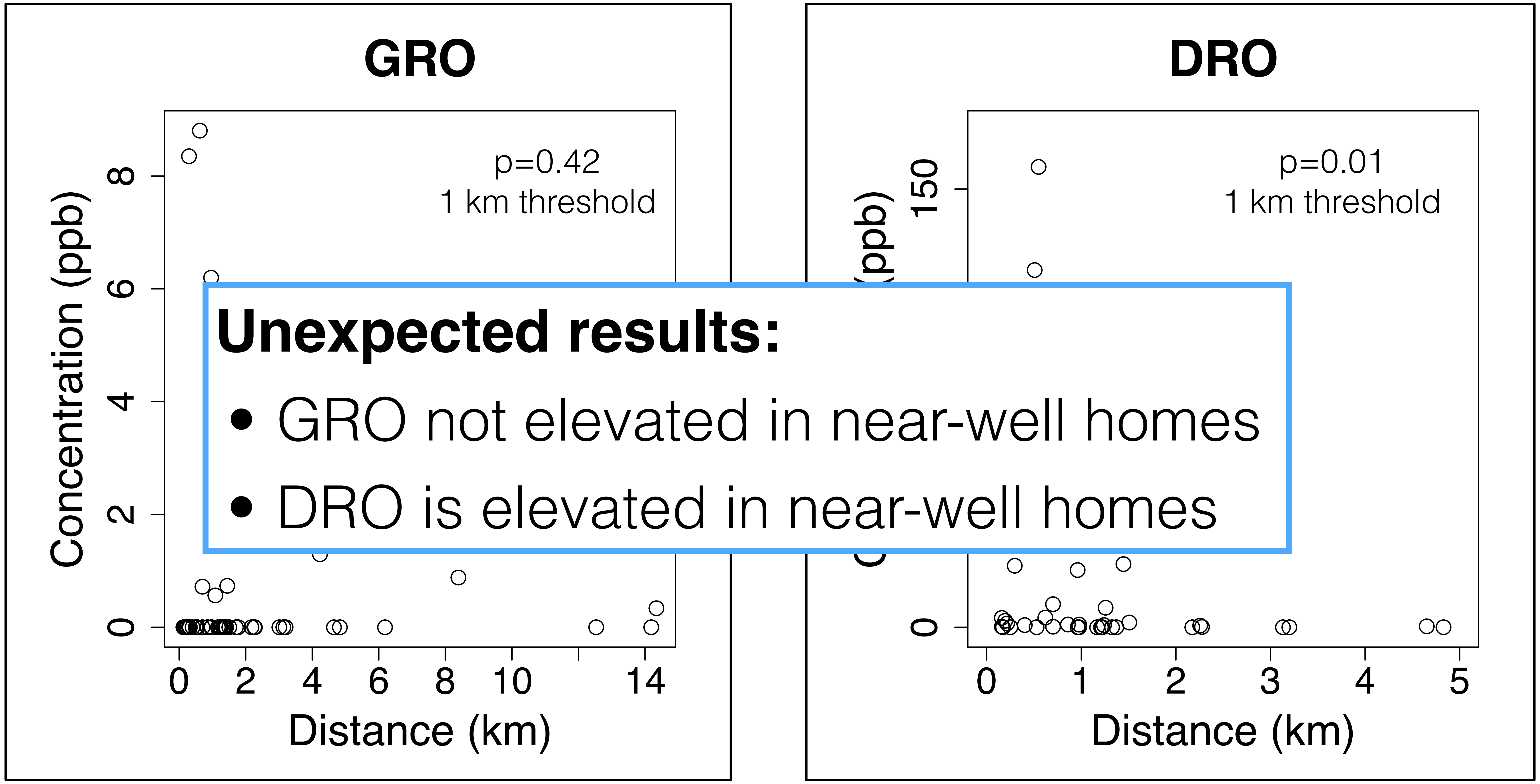
Hoelzer, Sumner, Plata et al. EST 2016

Evidence for organic chemical transport to groundwater?



- GRO: (2-methylpentane - 1,2,4-trimethylbenzene)
- DRO: (nC_{10}-nC_{28})
- compound-specific analysis (VOCs and higher boilers)

Proximity-to-well relationships



Unexpected results:

- GRO not elevated in near-well homes
- DRO is elevated in near-well homes

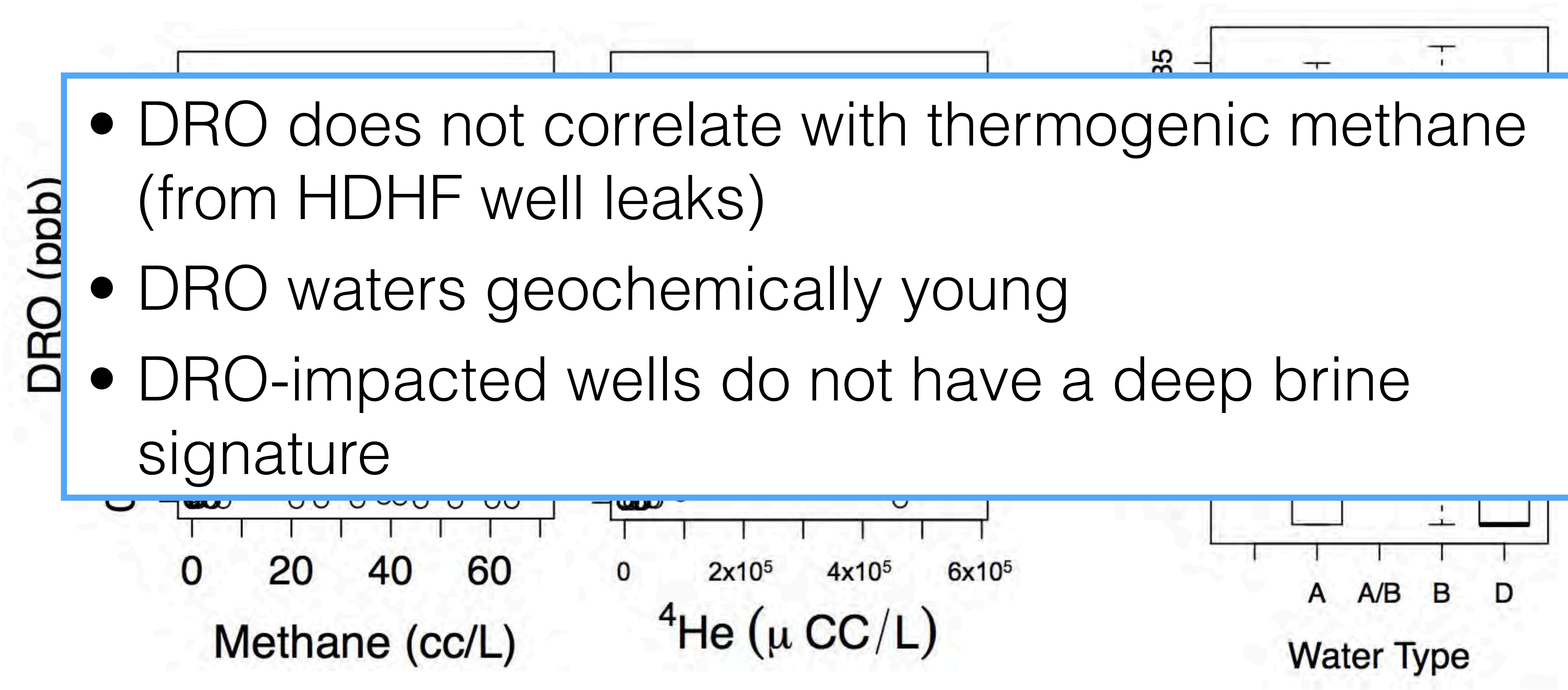
Drollette, Plata et al. PNAS 2015

Geochemical source indicators

Not from leaky casing

Geochemically young

High DRO lacks Marcellus brine signature

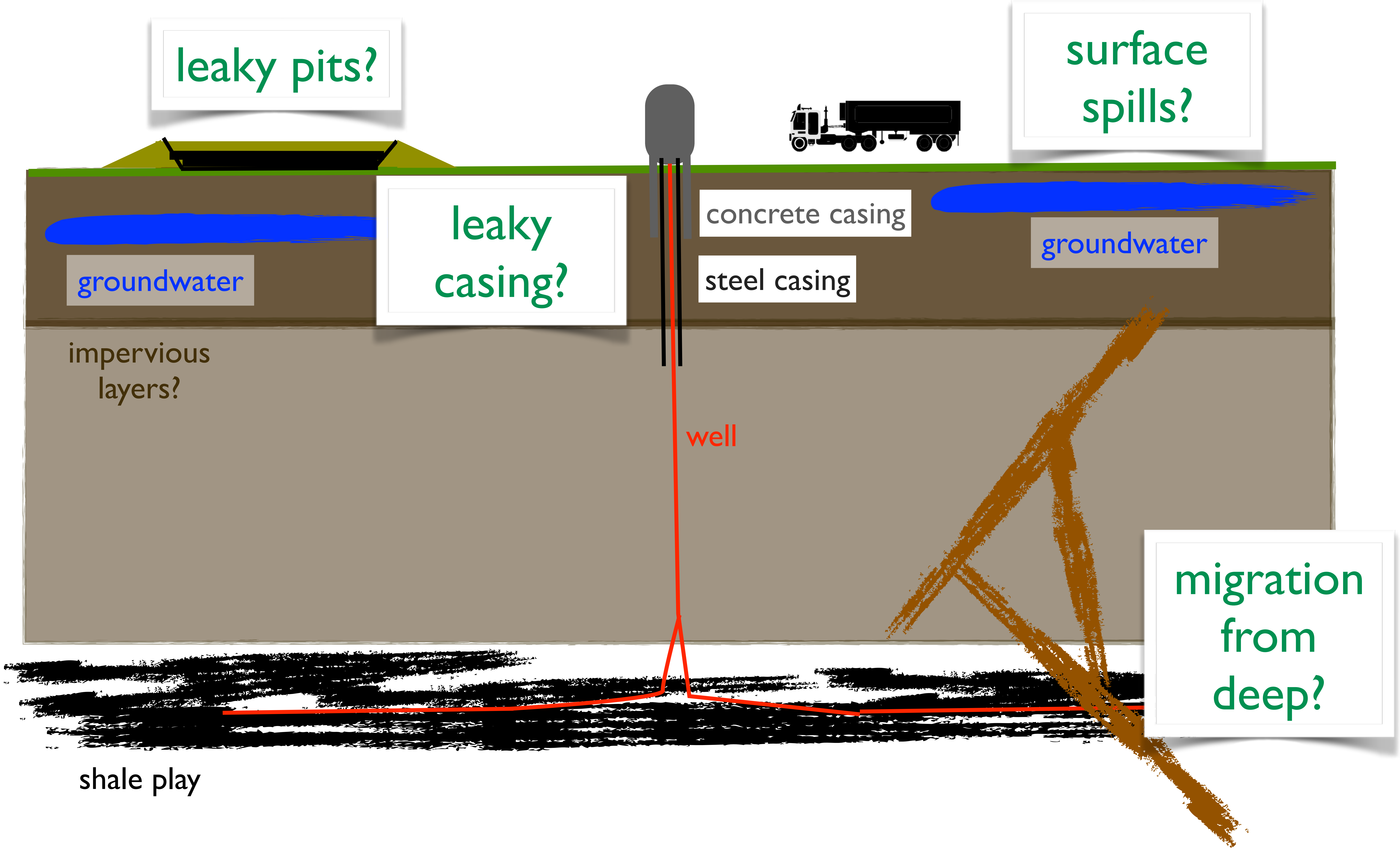


- DRO does not correlate with thermogenic methane (from HDHF well leaks)
- DRO waters geochemically young
- DRO-impacted wells do not have a deep brine signature

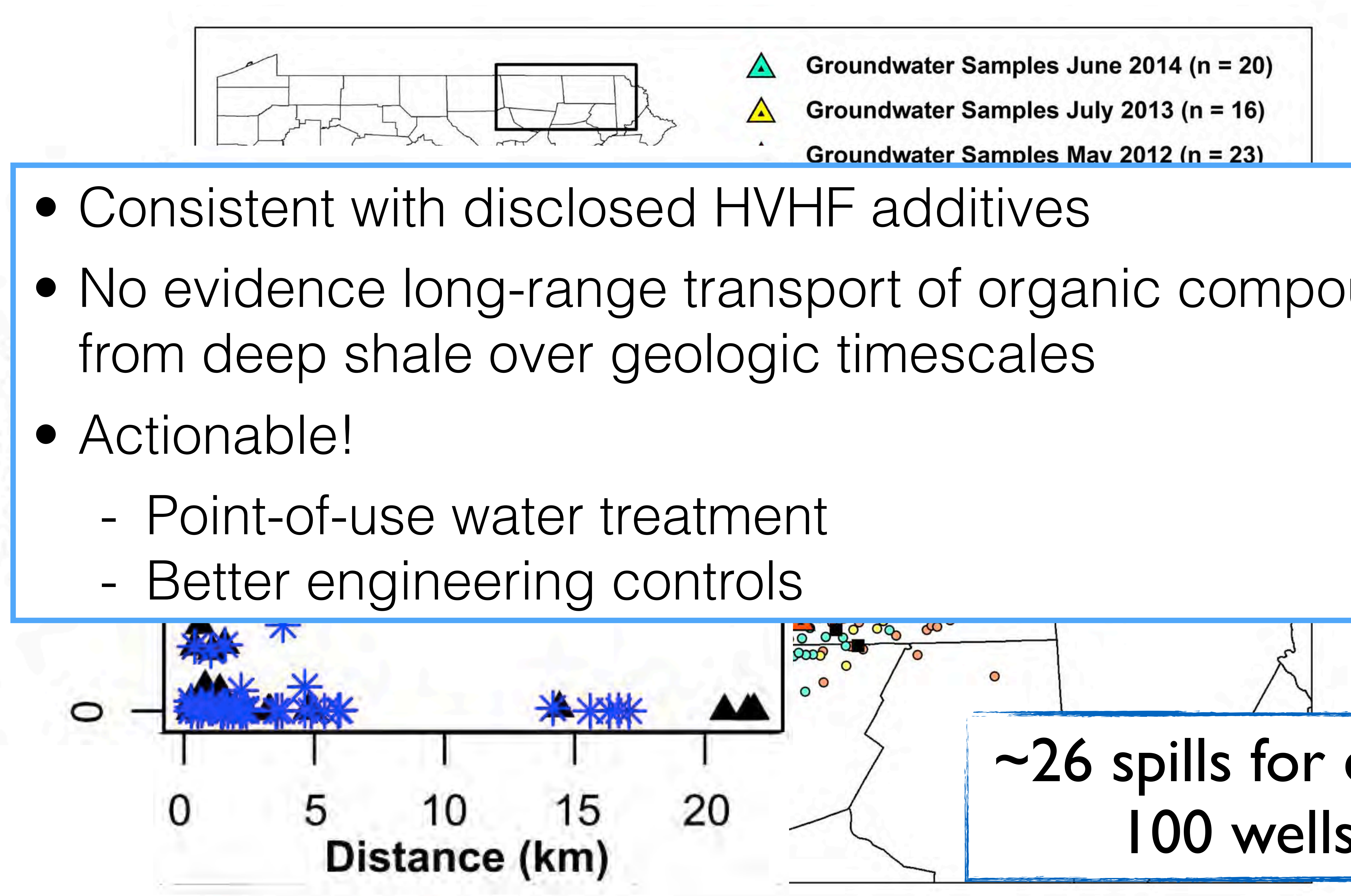
Type A: $CaHCO_3$ enriched
Type B: $NaHCO_3$ enriched
Type D: Cl^- enriched (Marcellus)

Drollette, Plata et al. PNAS 2015
Warner et al. PNAS 2012

Candidate sources for DRO without GRO



A surface-derived source: Accidents



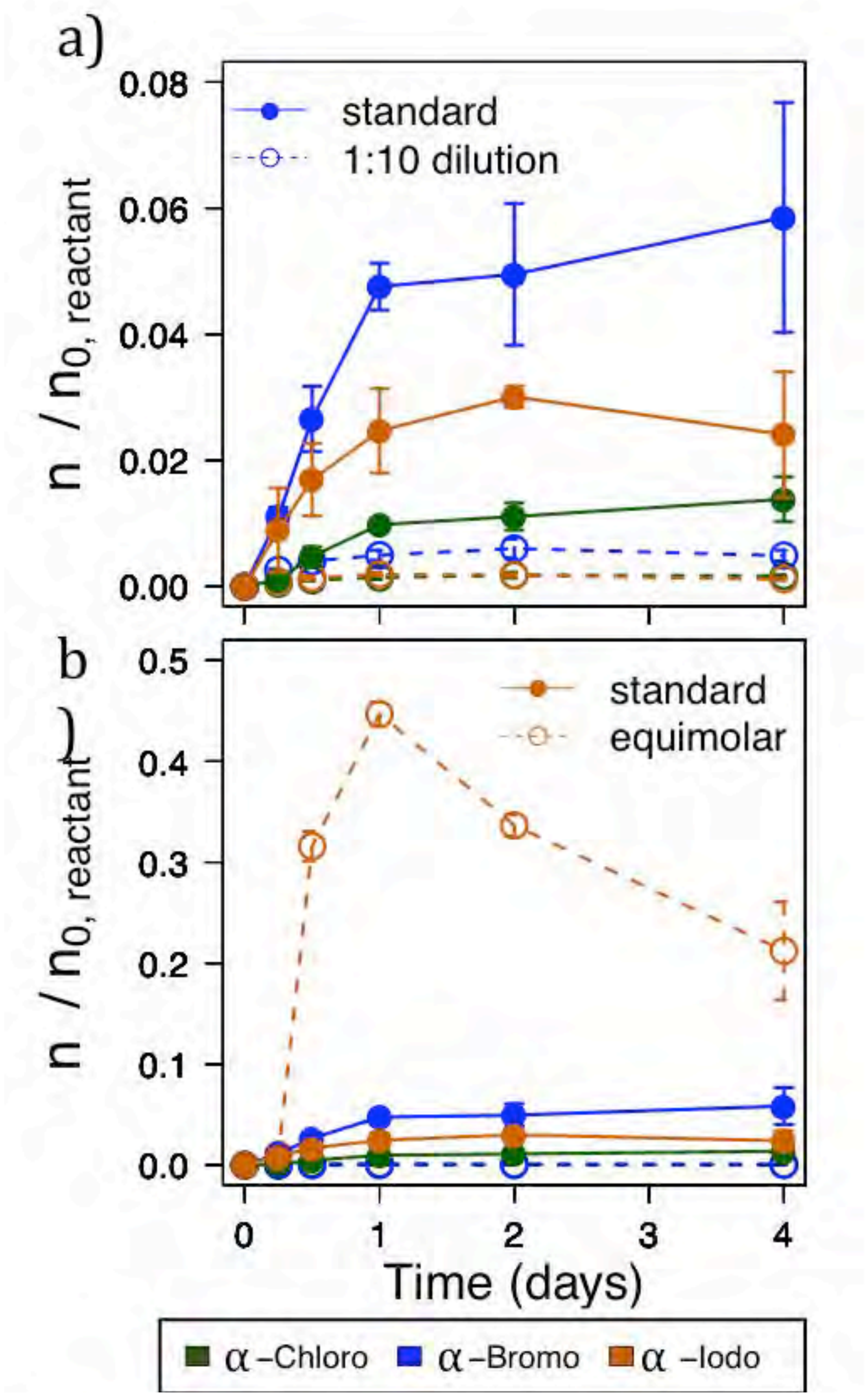
- Consistent with disclosed HVHF additives
- No evidence long-range transport of organic compounds from deep shale over geologic timescales
- Actionable!
  - Point-of-use water treatment
  - Better engineering controls

~26 spills for every 100 wells

Drollette, Plata et al. PNAS 2015

Mechanistic studies

Brine matters



Sumner and Plata, *EST*, 2018

Recall :
Nucleophilic substitution trend

I >	Br >	Cl >	H_2O
1	10	100	10,000

Oxidative trend
HOCl > HOBr > HOI

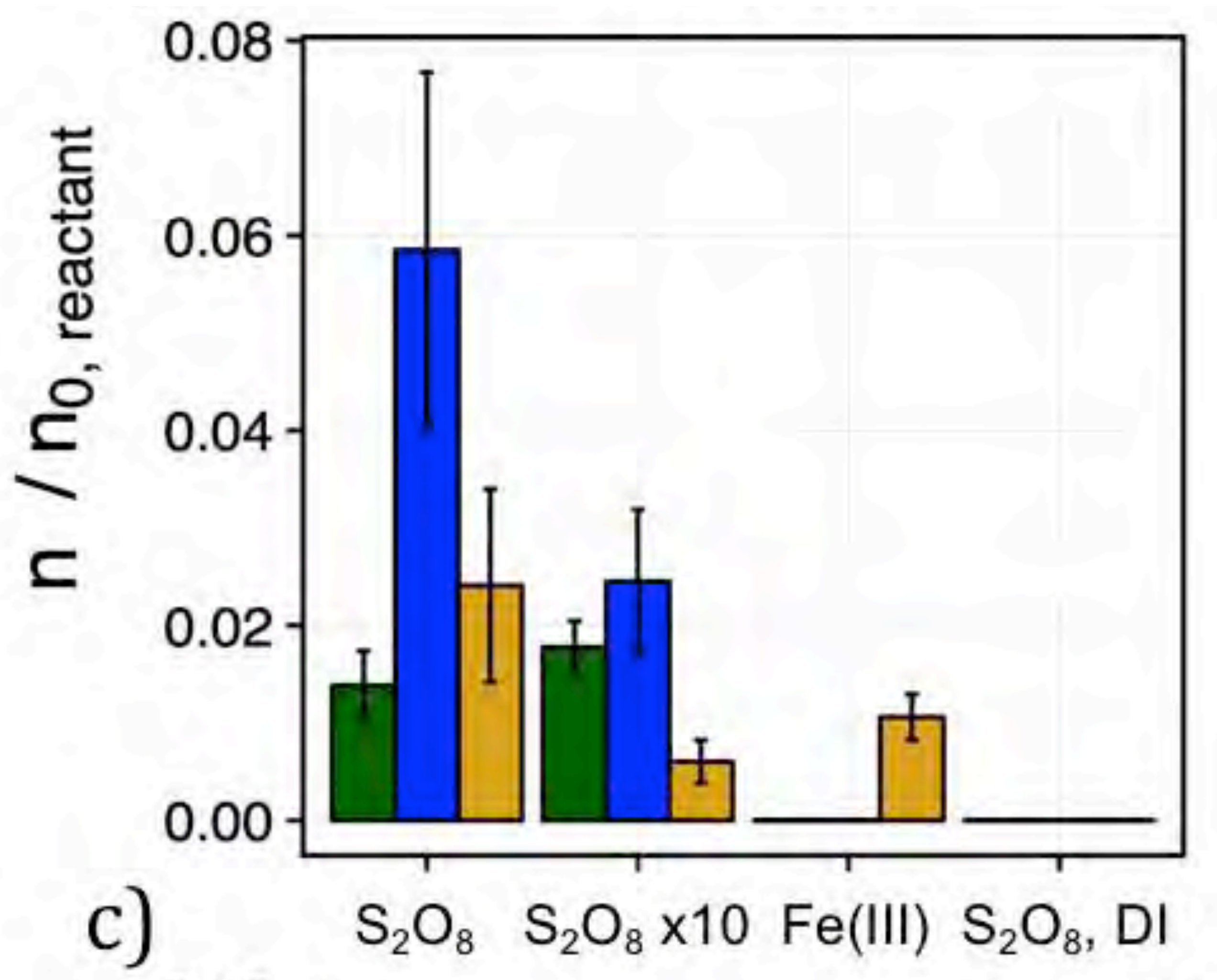
Redox favors formation of I_2

$$Cl_2 + 2Br^- \rightarrow 2Cl^- + Br_2$$

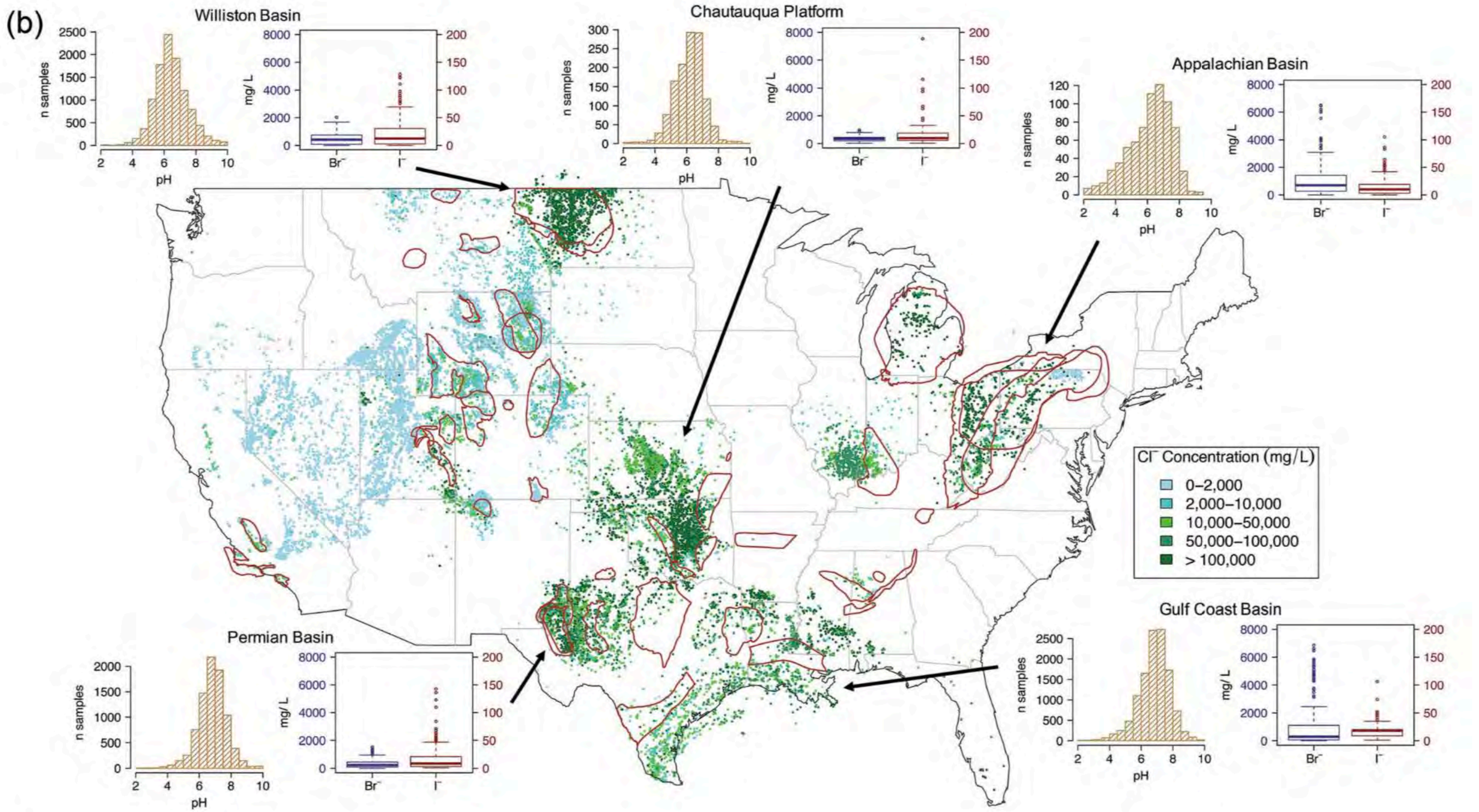
$$Cl_2 + 2I^- \rightarrow 2Cl^- + I_2$$

$$Br_2 + 2I^- \rightarrow 2Br^- + I_2$$

Oxidant matters



Brine composition



1 *(Cont.)*

Sumner and Plata, *Environ. Sci.: Processes & Impacts (ESPI)*, 2018

Are such transformations possible *in situ*?

Inorganic Composition

$Cl^- >> Br^- > I^-$

Temperature/ Pressure

T: 40 - 100°C (100 - 212°F)

P: 275 - 410 bar (4,000 – 6,000 psi)

Operator decisions

pH (1-7)

oxidant additions (persulfate, chlorite)

Sumner and Plata, *Environ. Sci.: Processes & Impacts (ESPI)*, 2018