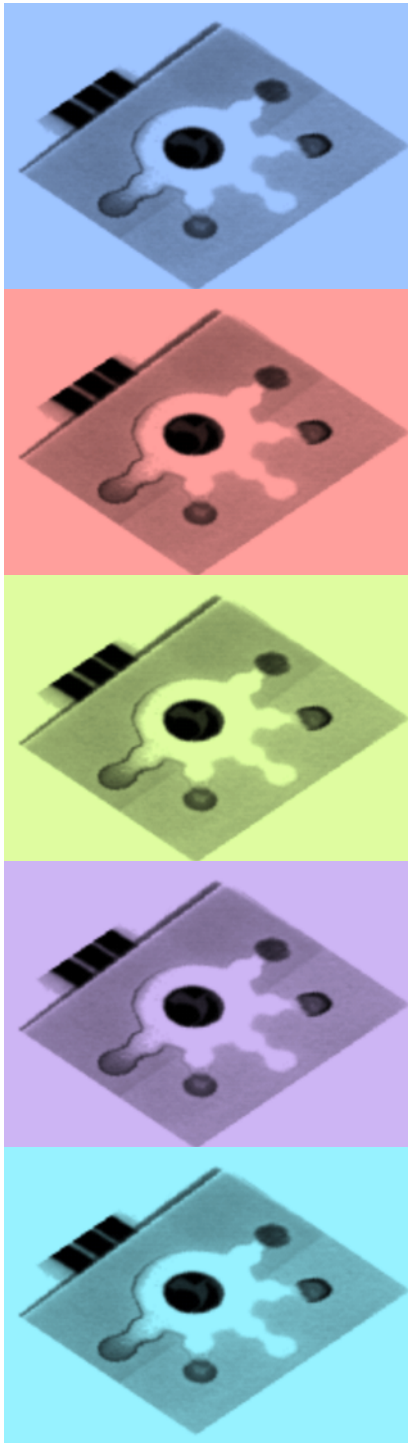


19th Century Innovations for 21st Century Exposure Science:

How Crayons, Paper, and Citizen-based Science Can Revolutionize Our Field

John Volckens

NEMC, 5 August 2014

Colorado State University

My Title Explained

19 Century Technology		21st Century Application
• Lithography	→	Rapid prototyping
• Litmus paper, wax	→	Paper-based microfluidics
• Pointillism	→	Chemical reagent printing

My talk in outline form:

Facts

Figures

Opinions

Fact #1:
Environmental Pollutant Concentrations Rarely Follow a Normal Distribution

and we've known this for a long time

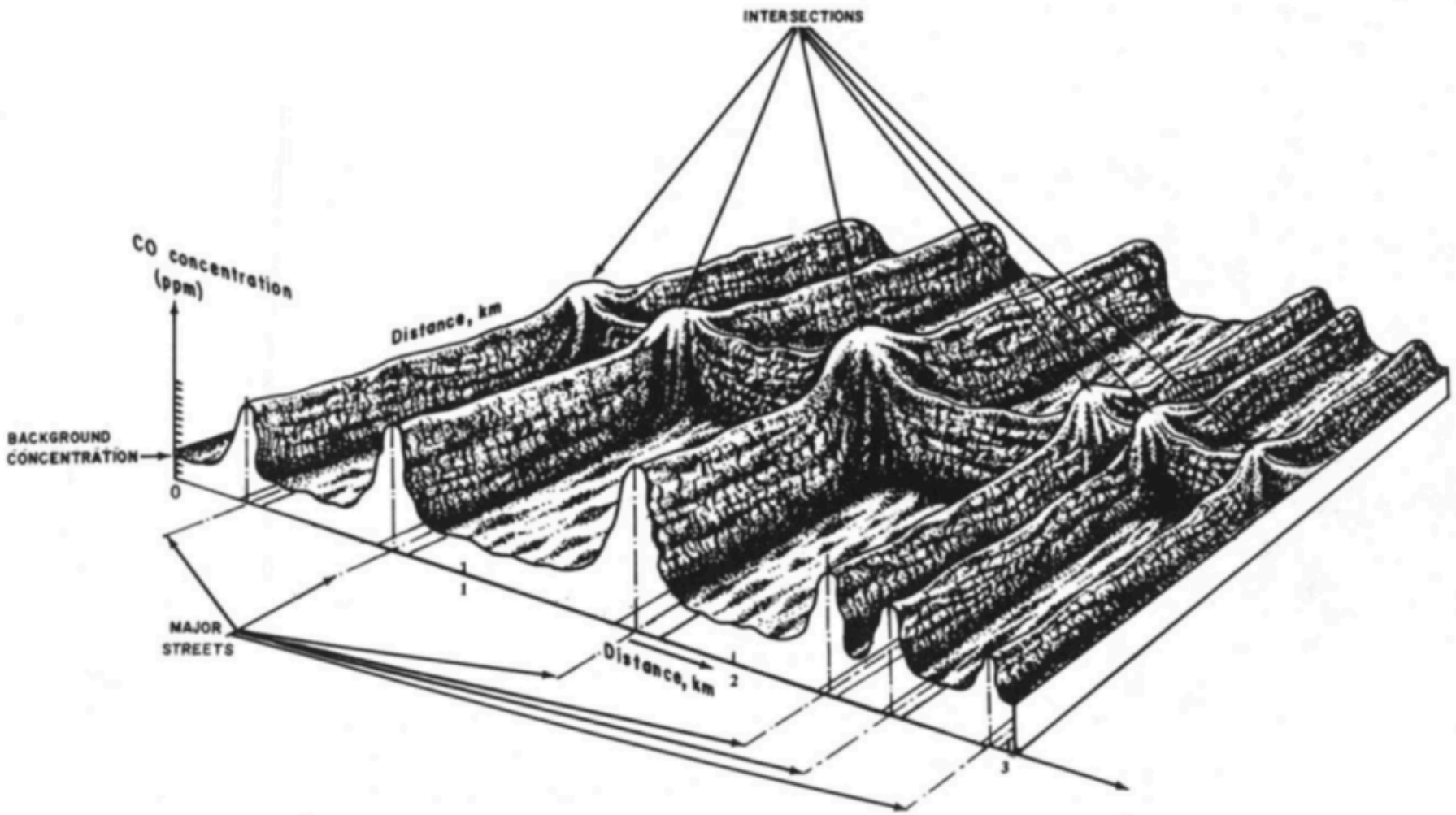


Fig. 3. Model of the spatial variation of carbon monoxide concentrations in a portion of an urban area measured at "breathing level" (approximately 2 m). The vertical axis denotes the concentration, and the horizontal axes denote distance across the city. (Source: Ott, 1977).

Ott, *Env. Int.* (1982) 7:179-196

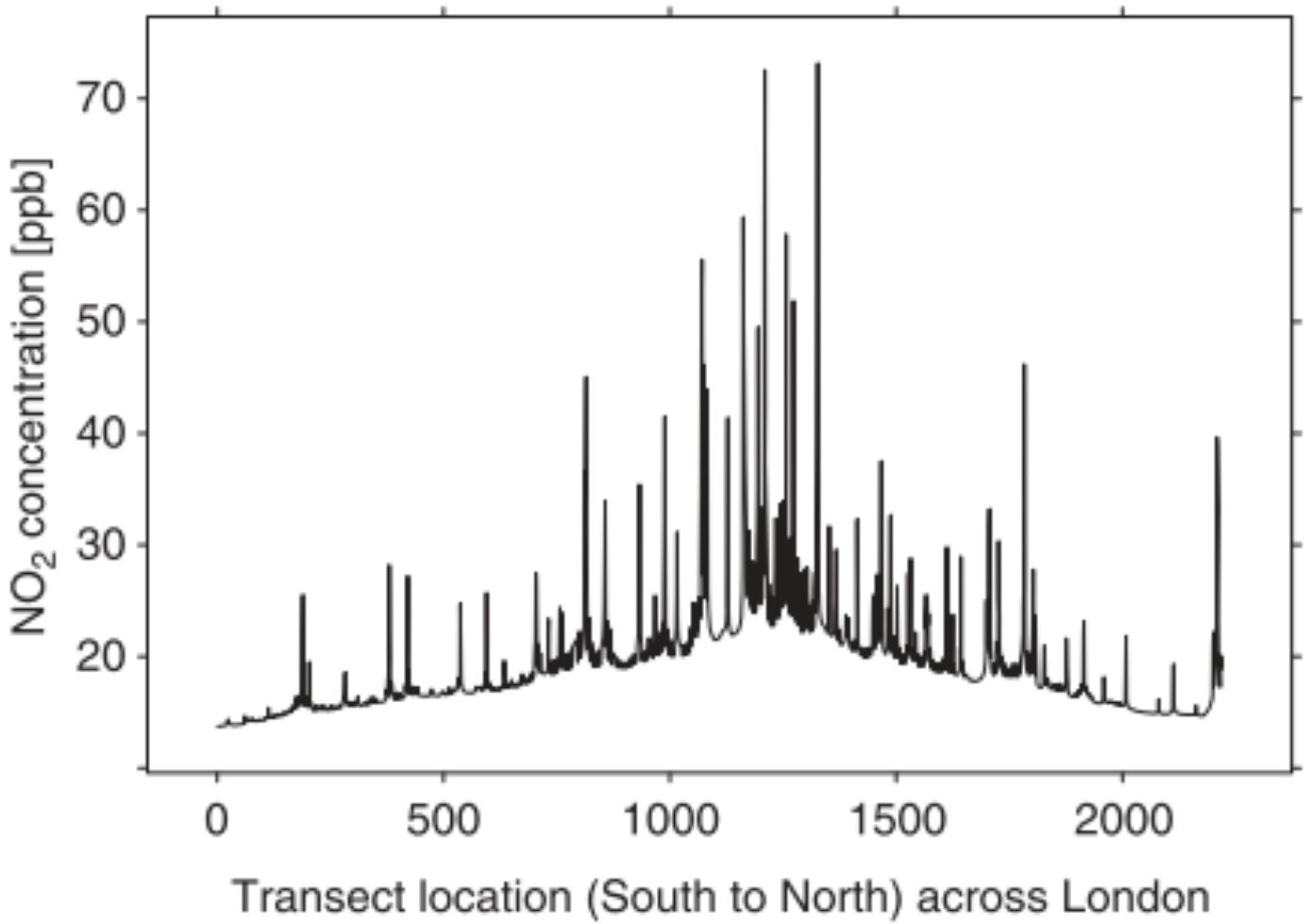


Figure 3. A transect of the annual mean NO_2 concentrations (parts per billion (p.p.b.)) for the year 2008 in London. The transect follows the vertical black line in Figure 2.

Beevers et al., *J. Exp. Sci. & Env. Epid.* (2013) **23,** 647–653

Fact #2:
Human Exposure to Environmental Pollutants Varies a Lot (often log-normally distributed)

MEASURING DUST EXPOSURE WITH THE THERMAL PRECIPITATOR IN COLLIERIES AND FOUNDRIES

BY

S. A. ROACH*

BJIM 16(4) 1959

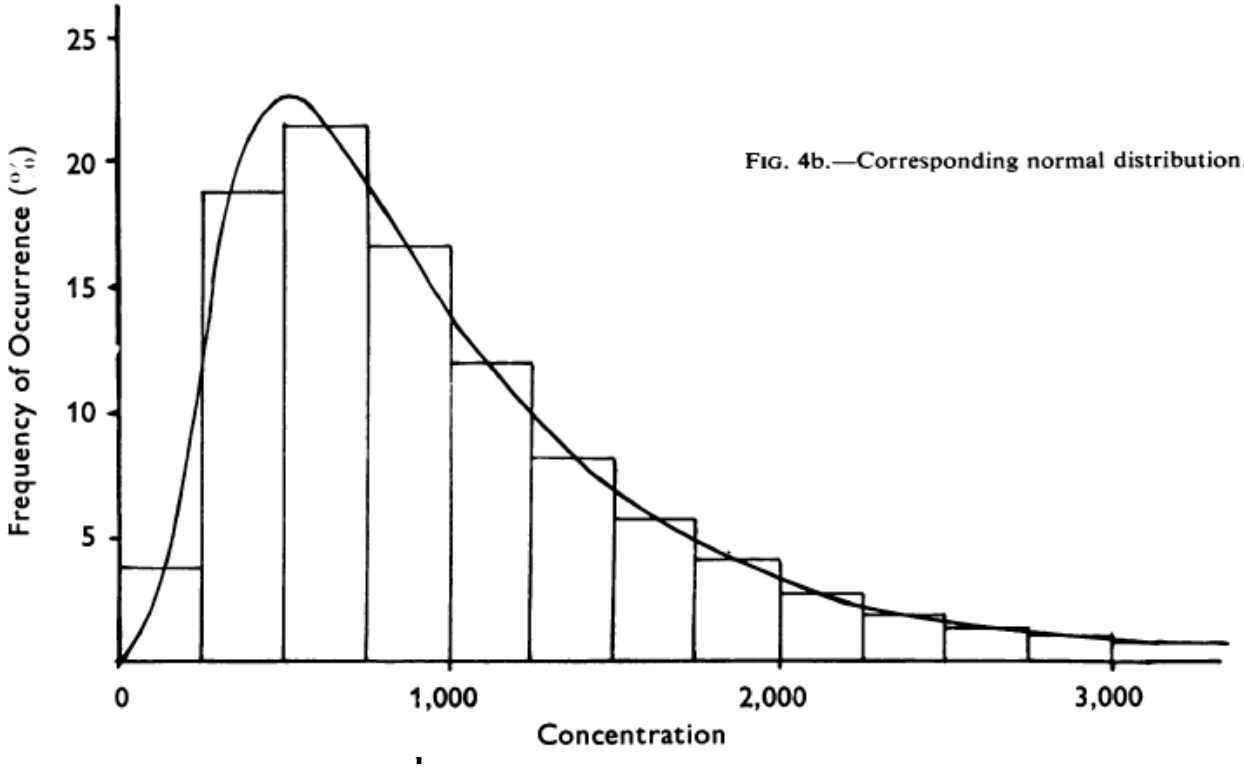
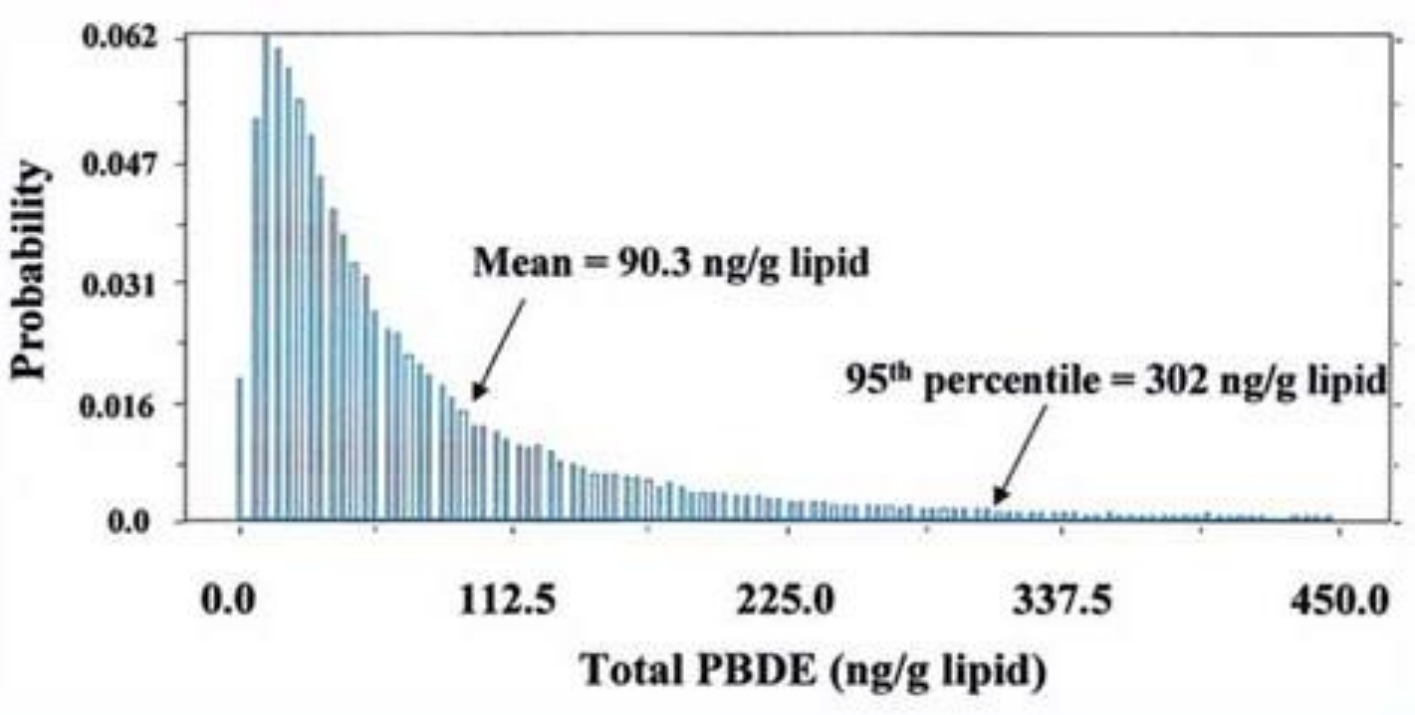


FIG. 4b.—Corresponding normal distribution.

Survey of PBDE Levels in Human Fat Tissue



Integrated Environmental Assessment and Management
Volume 1, Issue 4, pages 343-354, 5 NOV 2009 DOI: 10.1002/ieam.5630010404

So What?
What's Important about Log-Normal Data?

- Non-normal distributions are difficult to characterize from a sampling perspective

- How many samples are needed to characterize a log-normal distribution (μ, σ_g)?
  - Minimum of 30 samples *(Buringh, AIHAJ 1991)*

- How many samples are typically collected during a site visit?
  - OSHA 21D Consultation Programs: 0 – 3

Why Aren't We Taking More Measurements?

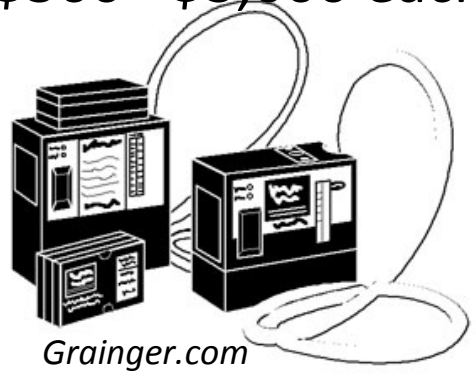
- We're lacking in resources:
  - Personnel
  - Time
  - Financial

Cost
State-of-the-Art for Metals: ICP-AES

- **Instrument cost:**
  - $50,000 - $150,000

- **Sample analysis cost:**
  - $100 for the first metal

- **Sampling Pumps:**
  - $500 - $3,000 each



Grainger.com

- **Personal Sampler:**
  - $100-$500

SKCinc.com

Cost Perspective

- The U.S. Census estimates a population of 466,400 welders, cutters, solderers, brazers nationally.

- Cost to measure each individual's exposure to one metal just once per year:
  - ~ $50M USD in analytical costs
  - ~ $10M in capital costs
  - ~ $10M in personnel costs

~$70M per year

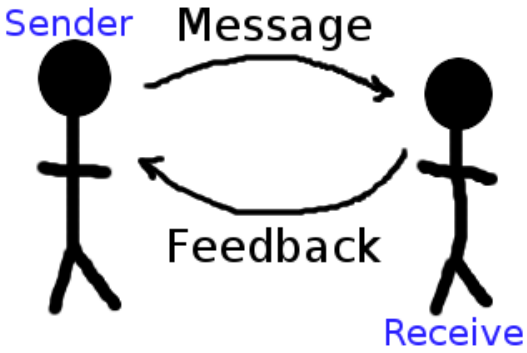
Time: At best, 2 weeks from Sampling to Results *(4 weeks is more common)*

Sampling: 1-2 days, pre/post

Shipping/Transport: 1 day

Sample analysis: 5 days

Data analysis: 1 day?



Risk Communication: 1 day

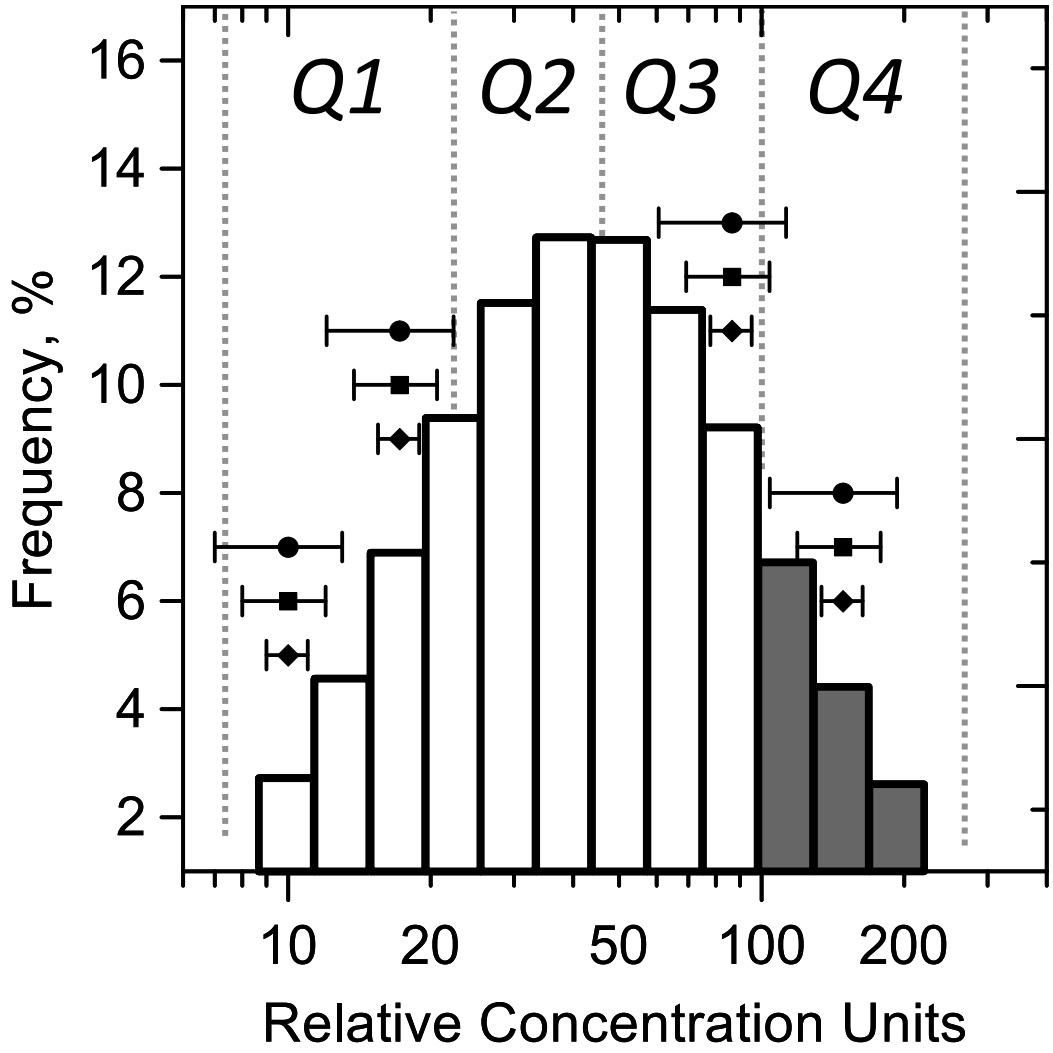
Environmental Measurement Capability: Wants vs. Needs

What we want

- Low Cost
- Highly Sensitive & Specific
- High Accuracy & Precision
- Portable
- Real-time
- GPS, Wi-Fi, Sunroof enabled

What we need: More Samples!

- Ultra-low cost
- Simple
- High Throughput
- Medium accuracy
- High specificity
- Medium sensitivity



Measurement Uncertainty

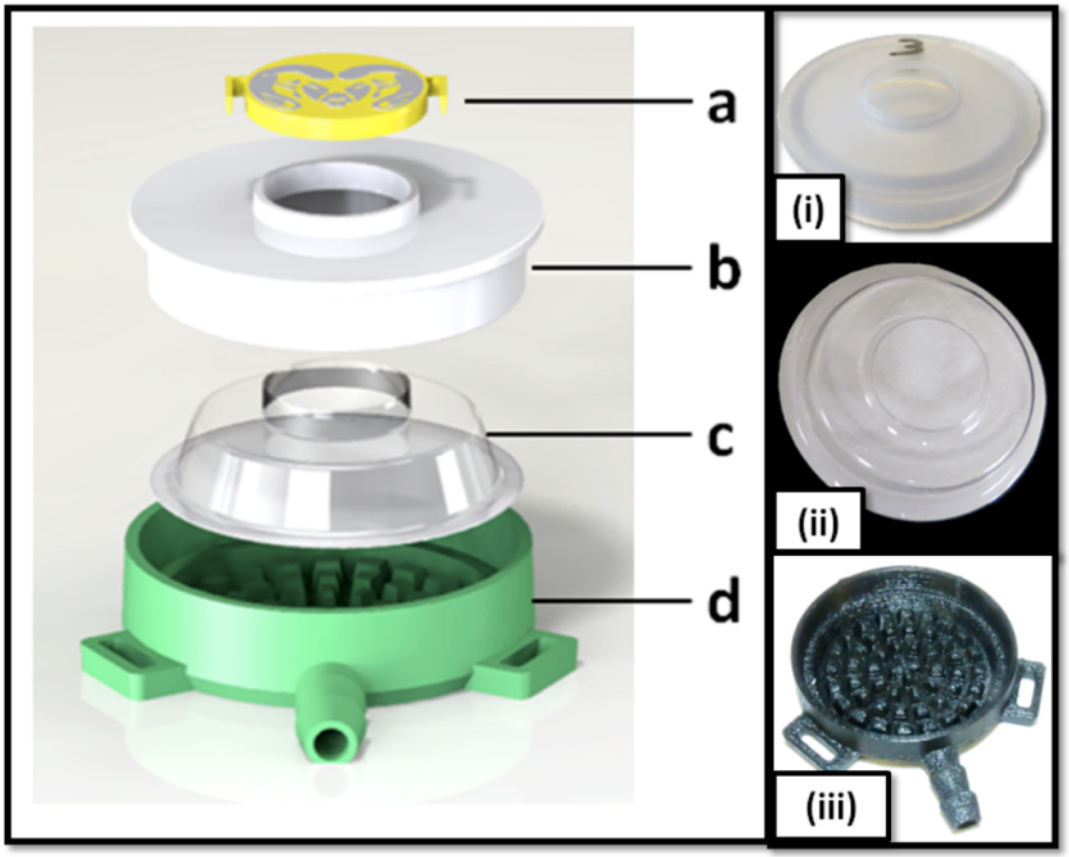
30%
20%
10%

Goal #1:
Lower the Cost of Sample Collection
(starting with personal air sampling)

Want a sampling apparatus that is:

- Inexpensive
- Disposable
- User friendly
- Reliable

The Answer in One Word?



1. Computer Aided Drawing
2. Rapid prototype via stereo lithography
3. Injection molded parts

Capsule Design and Fabrication

- Vacuum-formed polyethylene capsule (lightweight)
- Caps welded to filters using solvent (toluene)
- Wide range of bondable filter materials
- Low limit-of-detection

(gravimetric LOD: 10-25 µg)

L'Orange et al. *Ann Occ Hyg.* submitted

Air Sampling Pumps are NOT Cheap

- **Personal Sampling Pumps:**
  - $500 - $3,000 each!

Can we develop an alternative?

Sampling Pump Design Options

Axial/Radial Fan

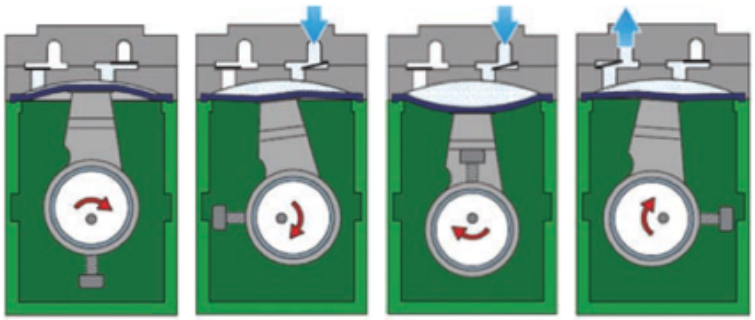
- Simple
- Inexpensive
- Mass-produced

- Poor pressure performance
- Easily fouled

Diaphragm Pump

- Good pressure performance
- Proven technology

- Many parts
- Expensive
- Pulsing flow



Ultrasonic Pump

- Fair pressure performance
- Inexpensive
- Silent

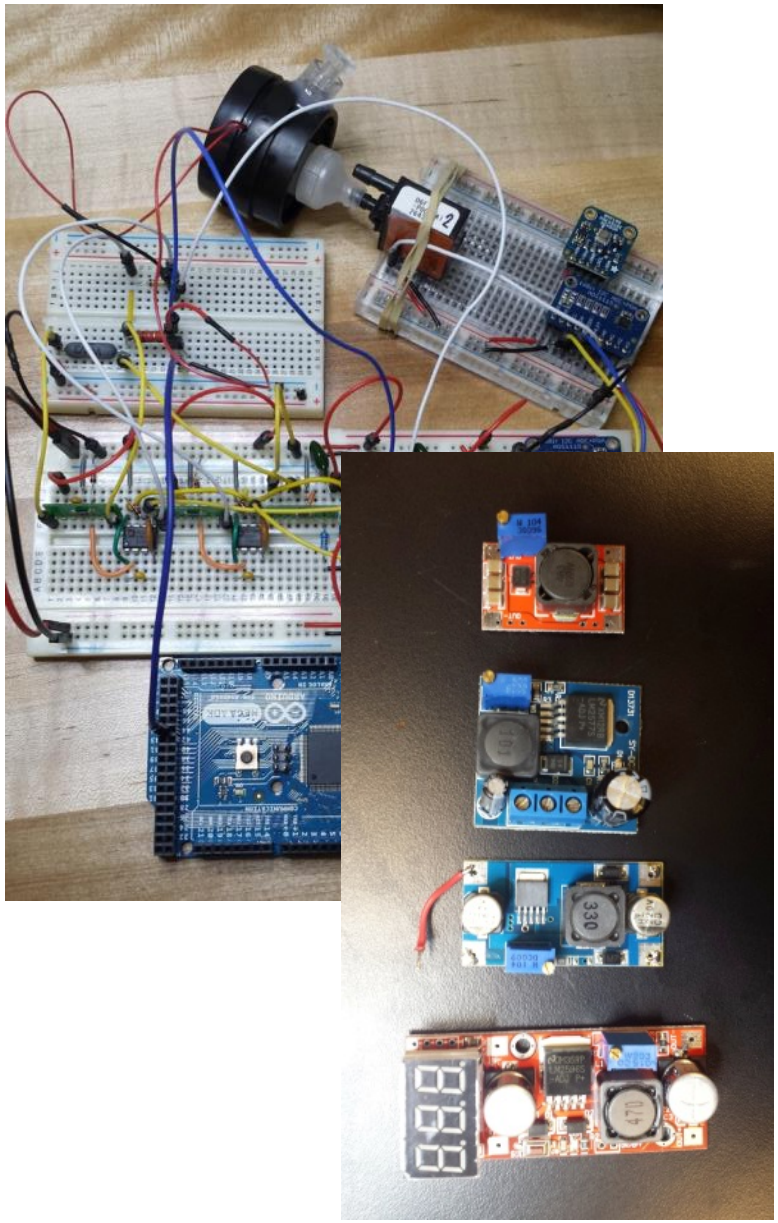
- Untested…
- Adequate pressure performance?

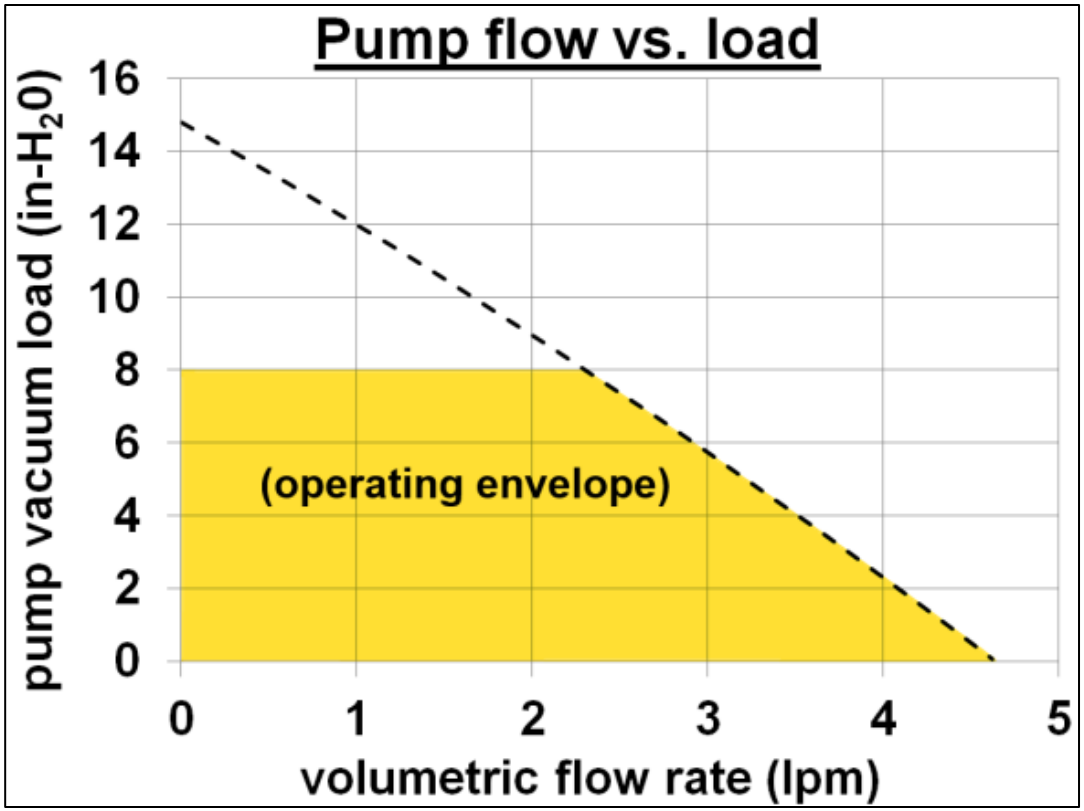
Arduino-based, Rapid-Prototype, Personal Ultrasonic Sampling Pump (1-4 Lpm)

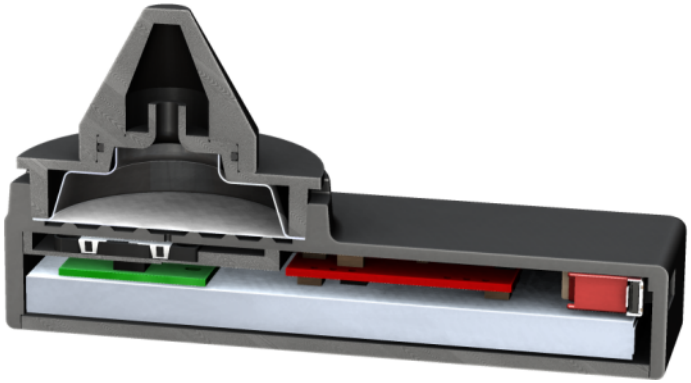
CAD Model ➔ Rapid Prototype Housing & Electronics

After 2 days and $300 we have a prototype made by stereo lithography

Low-Volume Ultrasonic Air Sampler







Bill of Materials for Prototype Air Sampler

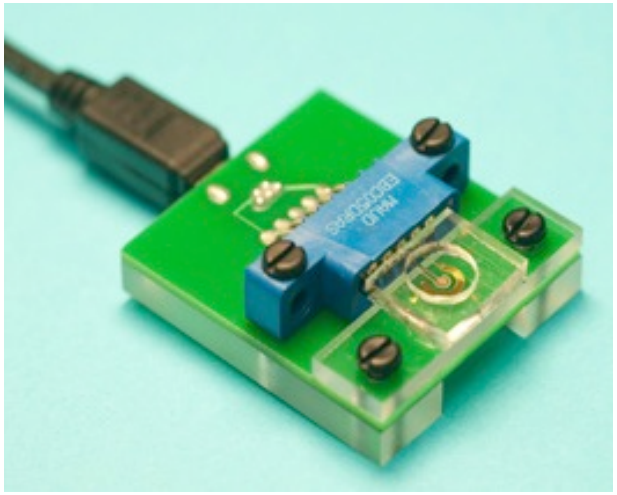
Component	Prototype Costs (USD)	Volume Production (USD)
Housing	$200	$5
Pump	$30	$10
Circuit/Wiring	$60	$5
Battery	$25	$10
Bluetooth	$10	$3
Hardware	$10	$2
TOTAL	**$335**	**$35 (est.)**

Goal #2:
Lower the Cost of Sample Analysis

Wikipedia.org

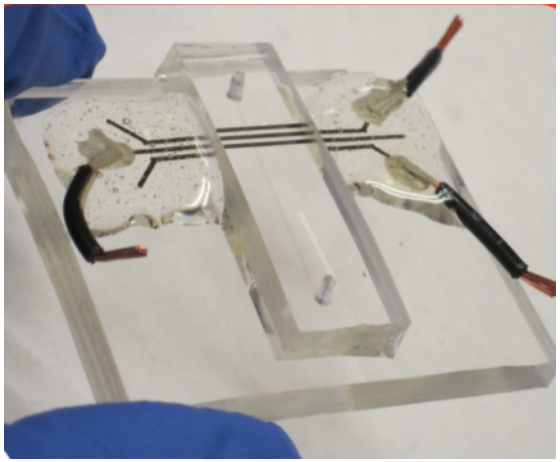
Microfluidics?

- Microfluidics is analytic chemistry using sample volumes on the order of *microliters* instead of milliliters
- **Why are we interested in microfluidics?**
  - Small quantities of reagents (lab on a chip)
    - Same sample analyzed in less volume -> increased sensitivity
  - Low cost and fast analysis



Manganese in blood[1]

Electrospray LC-MS[2]



Aerosol Reactivity[3]

[1]Jothimuthu P, *et. al. Lab on a Chip* (2011) [2] www.agilent.com [3] Sameenoi , *et al. JACS* (2012)

Microfluidics on Paper?

- **Microfluidic Paper-based Analytical Devices (mPADS)**
  - Paper patterned with wax (or other hydrophobic material)
  - Liquid transport by capillary action
  - Flow circuits designed for in-situ chemistry

- **Rapidly Growing Field**
  - Mostly biological applications to date

Whitesides, G. M. et al. *Bioassays,* 2007,

Dungchai et al. *Anal. Chim. Acta 2010*

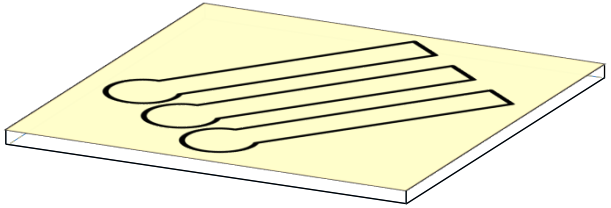
Advantages of mPAD Technology

- VERY inexpensive (less than 5¢ per device)
- Portable and disposable
- Easy to make, easy to use
- Rapid analysis (minutes)

Xerox Colorqube 8870

Epson R280

Print wax barrier

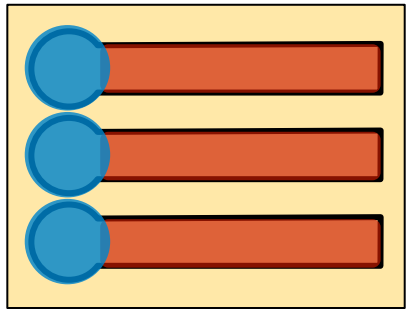


Melt wax barrier

Heat

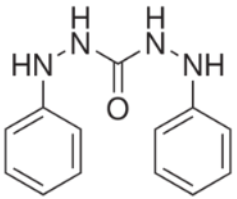
Detection regions

Pre-treatment zones

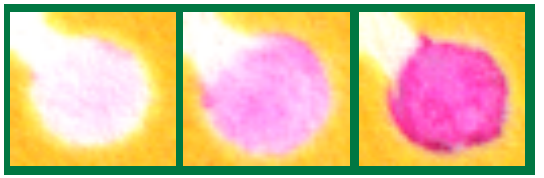


Many Applications for Environmental Monitoring

Inorganics [1]

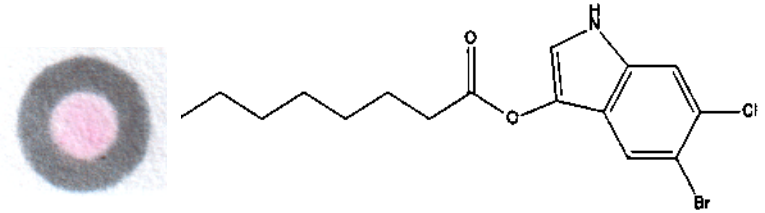


Chromium-VI + 1,5-Diphenylcarbazide →

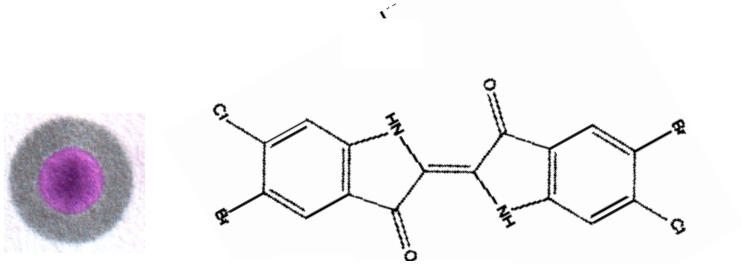


0.12 µg **1.5 µg** **6 µg**

Microorganisms [2]



esterase →



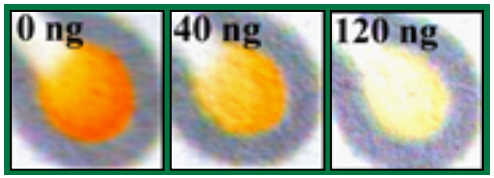
Magenta Caprylate

Salmonella Detection

Organics [3]

$PM_{2.5}$ + Dithiothreitol

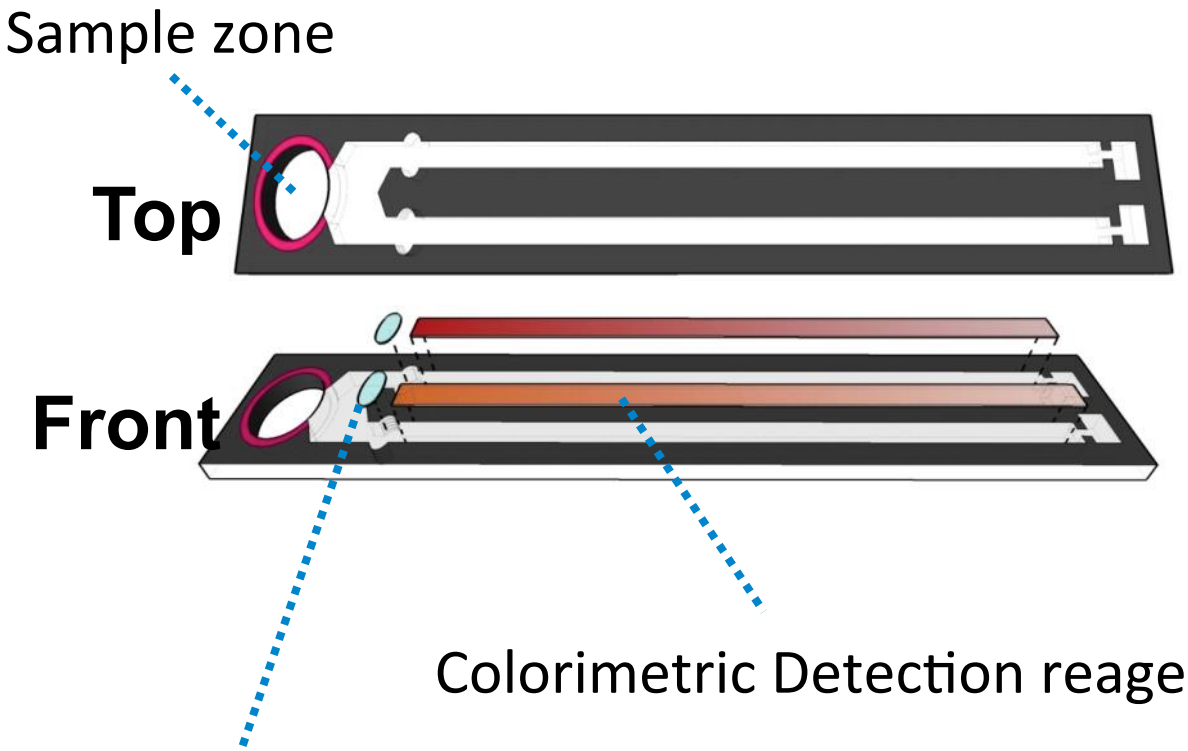
DTNB →

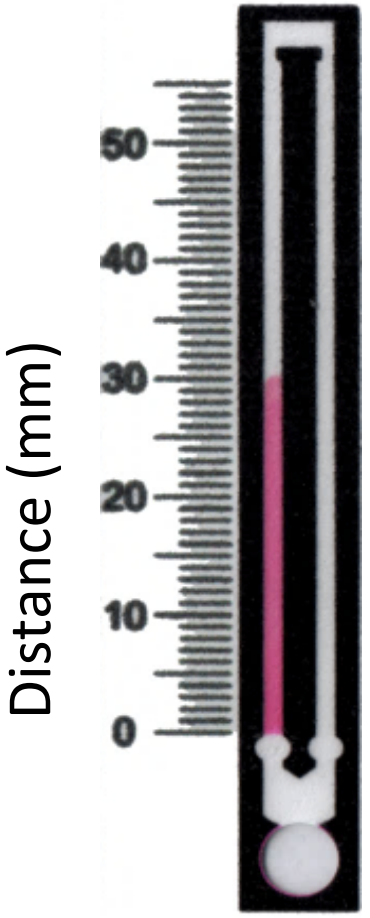


Aerosol ROS

(1) Mentele et al. *Anal Chem.* (2012) 84, 4474−4480; (2) Jokerst et al. *Anal. Chem.*, (2012), *84* (6), pp 2900–2907
(3) Sameenoi et al. *Environ. Sci. Tech. (*2013), *47* (2), pp 932–940

Distance-Based Detection: Simple, portable unpowered, rapid analysis, μg (ppm) resolution

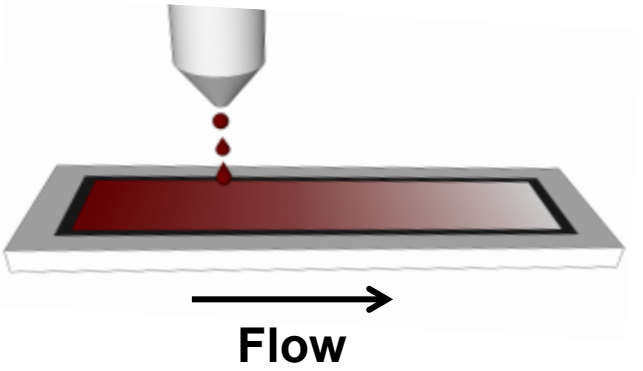


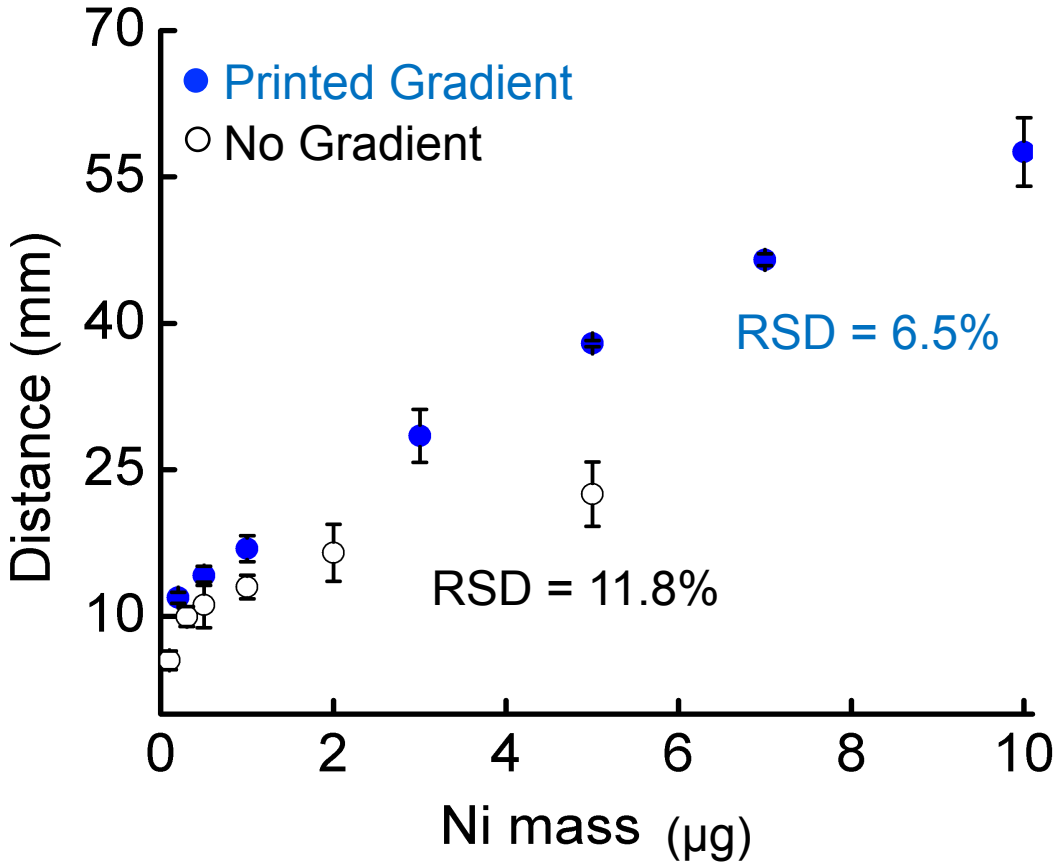


15 μg Ni

Inkjet Printing: Reagent Gradients

Gradient of Dimethylglyoxime



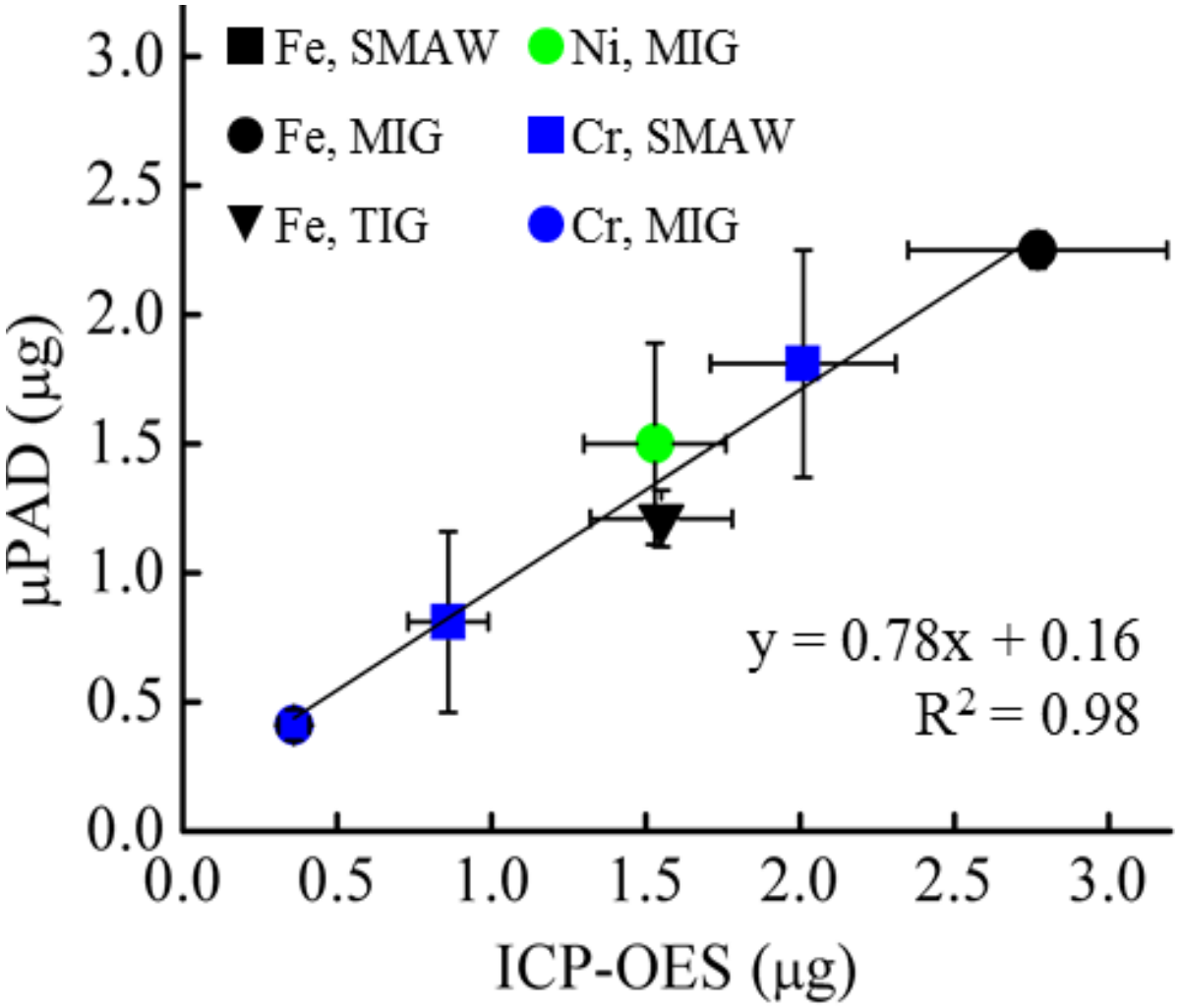


Precise reagent printing creates a linear response curve with improved dynamic range

Multiplexed Analysis of Cu, Fe in Welding Fume

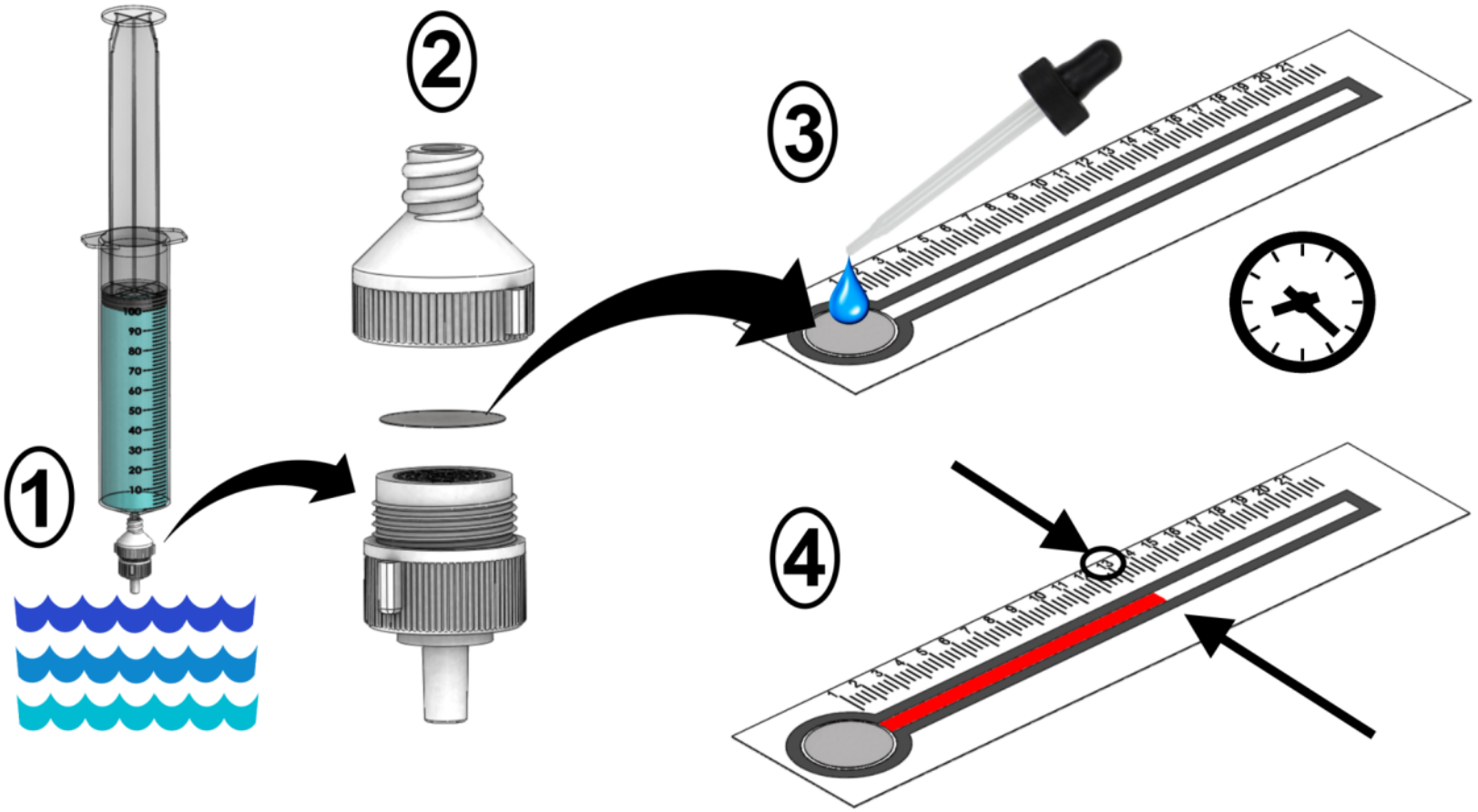
- Remove punch (10mm) from sampling filter
- Add 5 µL HNO_3 to digest metals
- Microwave for ~30 sec
- Neutralize sample with 8 µL $NaHCO_3$
- Place punch on µPAD
- Elute metals with 30 µL H_20
- Measure color change/intensity

Metals in Welding Fume: mPAD vs. ICP-AES

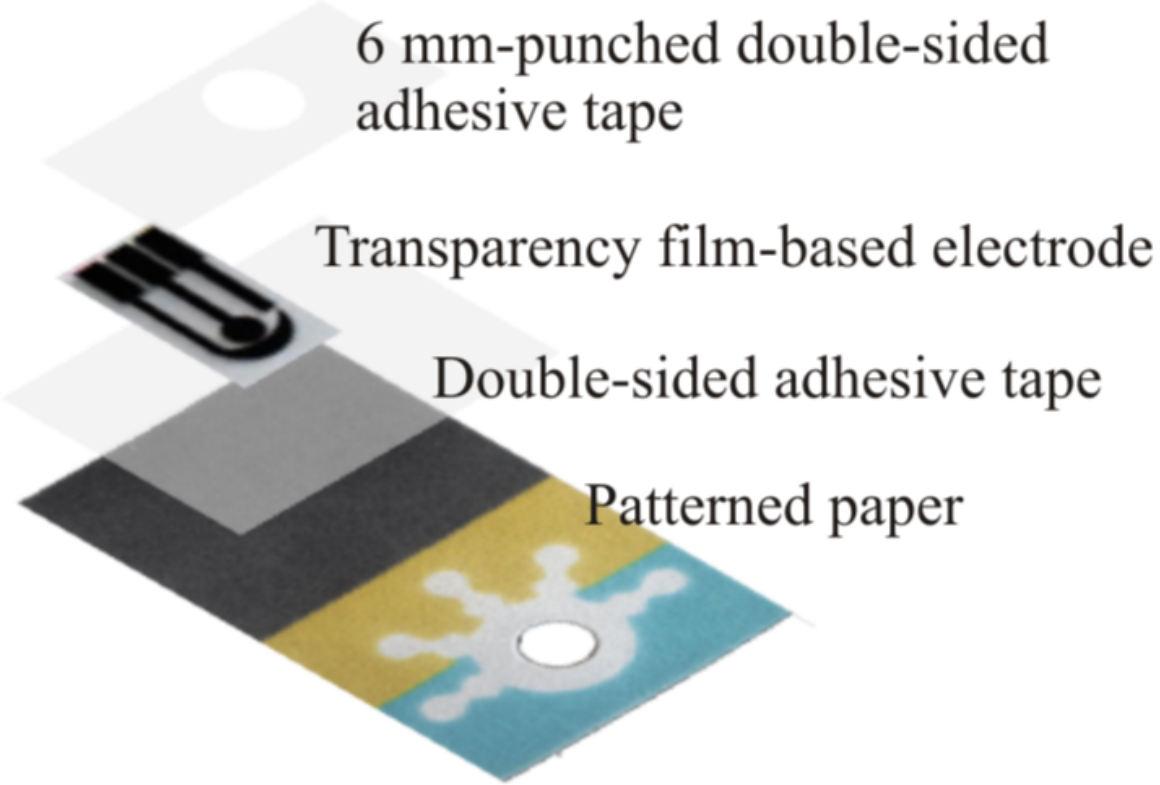


Cate et al. *Annals of Occ. Hyg.* (2014) 58 (4): 413-423

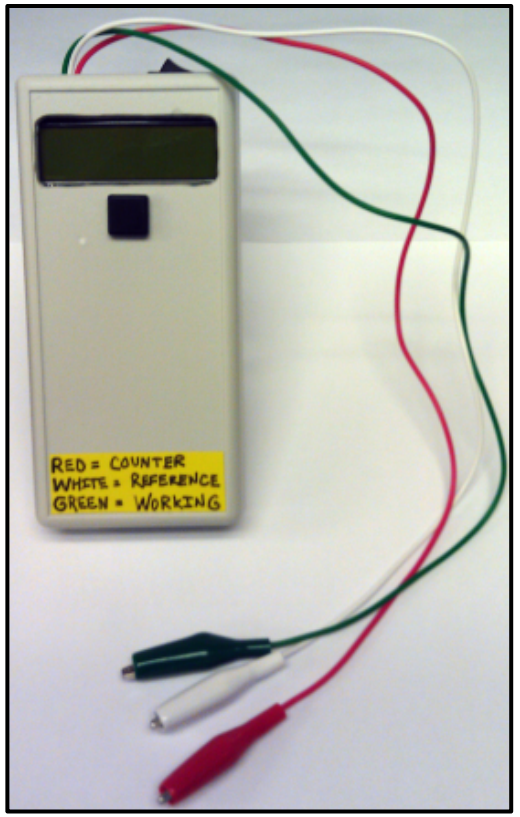
Application to Metals in Water



Colorimetric Detection Paper: 0.1 μg Sensitivity
Electrochemical Detection on Paper: 1 ng Sensitivity

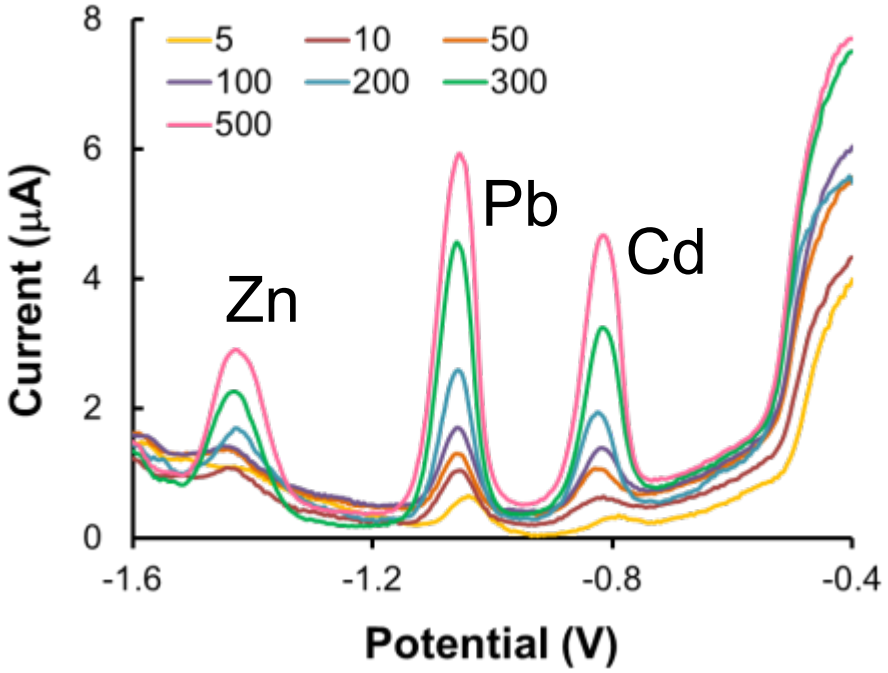


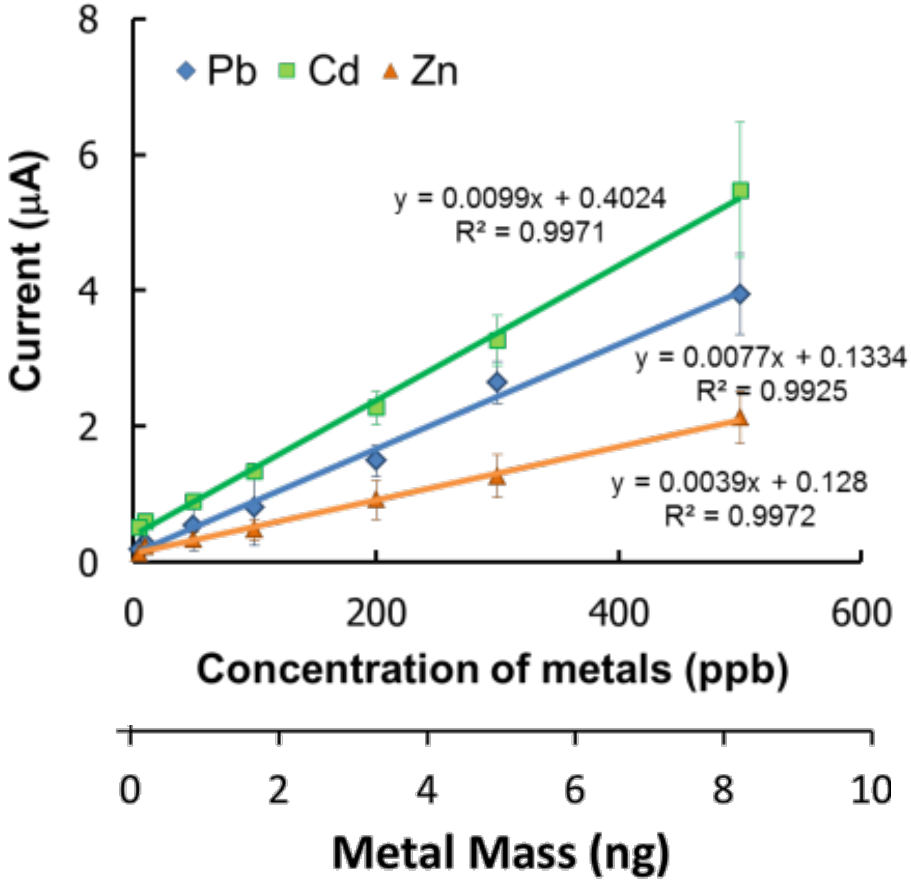
Rattanarnat et al. *Anal. Chem.*, (2014), *86* (7), pp 3555–3562



Rowe et al. *Plos One* (2011)
DOI: 10.1371/journal.pone.0023783

Electrochemical Detection of Cd, Pb, and Zn in Air and Water



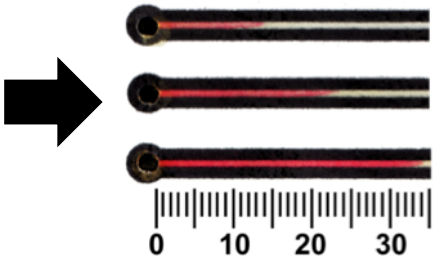


Making Low-Cost Environmental Measurements a Reality

Measurement

$25

Analysis



$2

Interpretation

You $$$

Opinion #1

Low-Cost Technologies (and Citizen Science) Will Never Replace You or the State-of-the-Art

Technology to Empower Awareness, Knowledge, Action

- 100 years ago you went to the doctor to have your temperature taken

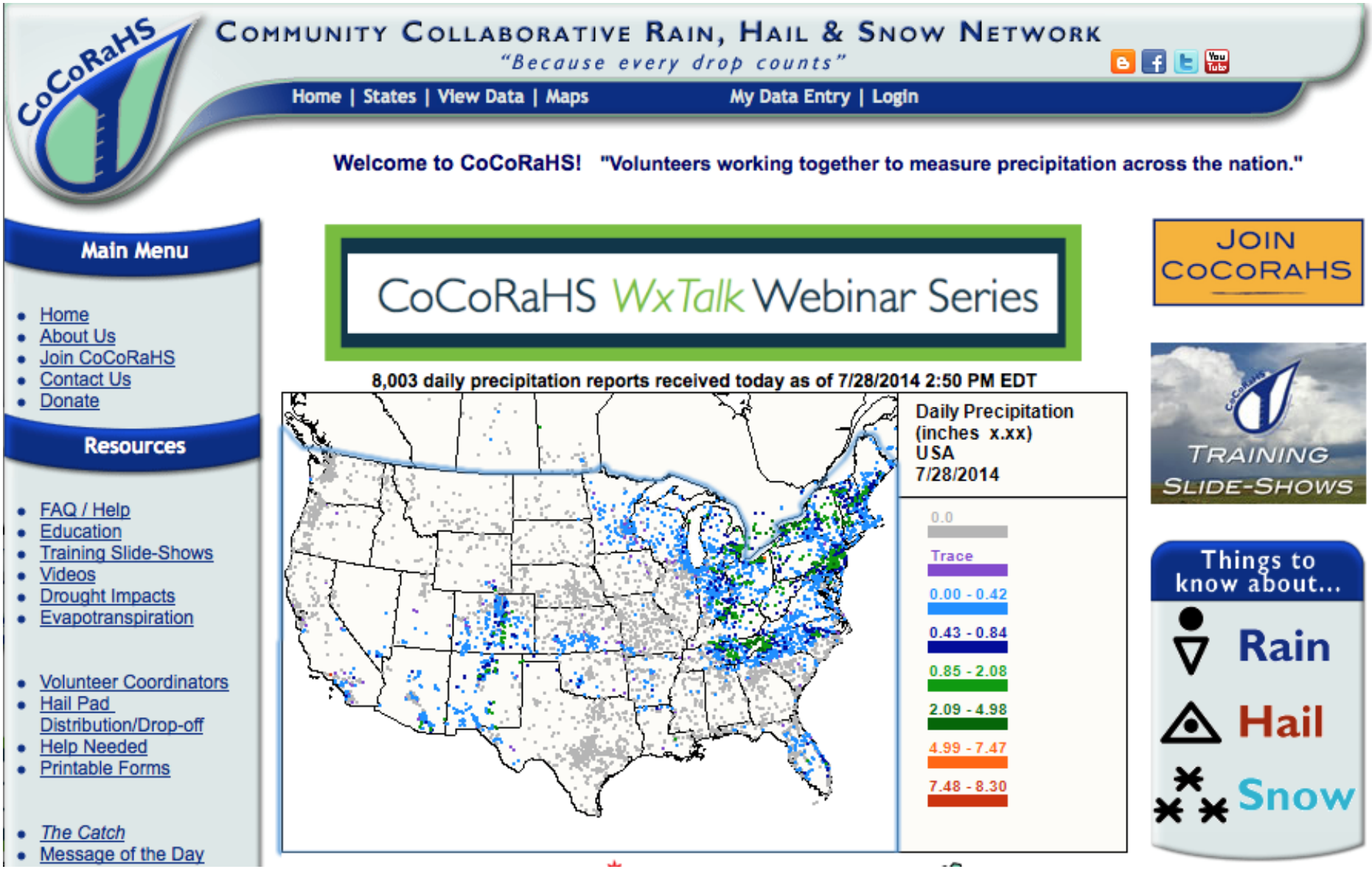
- 25 years ago you did the same to find out if you were pregnant

- 10 years ago you needed official credentials to be called a journalist

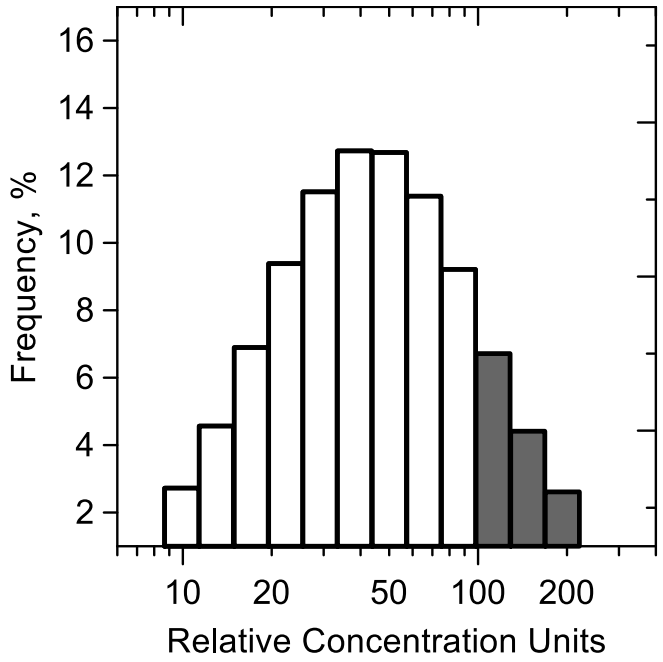
Opinion #2

Larger sample sizes reduce our reliance on precision and improve our ability to problem solve

Citizen-Science Can Pay Big Dividends



Opinion #3



Not all monitoring needs to be 'regulatory-driven'

Environmental measurements should support problem finding and problem solving

Opinion #4

“Real-time” measurements are great but they are overstated and overrated relative to our needs

‘Same-day’ is plenty fine for many applications

Acknowledgements

Colorado State University

Prof Chuck Henry

Dr. Kim Anderson
Dr. Mallory Mentele (Regis University)
Dr. Christian L'Orange
Dr. Kirsten Koehler (Johns Hopkins)
Dr. Yupaporn Sameenoi (Burapha University)
David Cate
Jaclyn Adkins
Poormat Rattanarat
Dan Miller-Lionberg
Casey Quinn
Nathan Henry

Funding

NIOSH R01OH010295
NIEHS R21ES019264
NIOSH R21OH010050

john.volckens@colostate.edu