Chemical Analysis versus Bioassay

S16a

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Ching Lo, James Li

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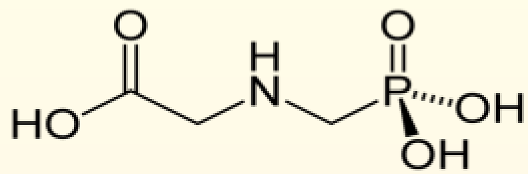
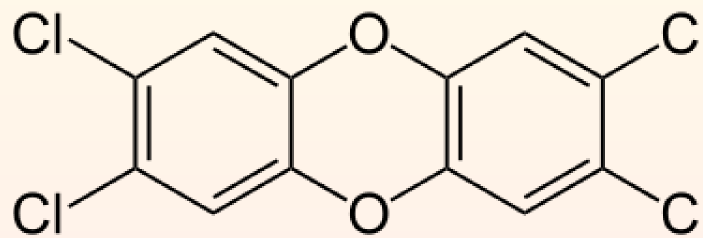
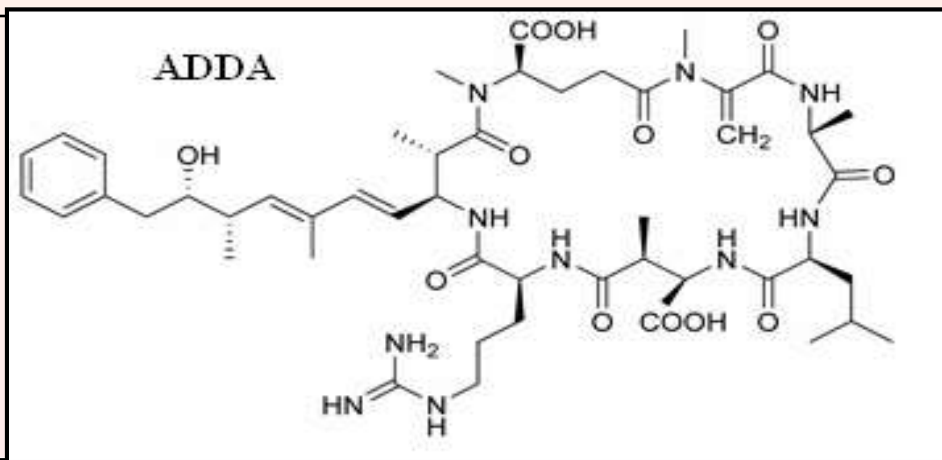
Chemical analysis versus bioassay for environmental analysis of hazardous organic compounds: when to use what?

Three categories of environmental pollutants as study models

1. Pesticides/herbicides — glyphosate {a single chemical configuration}
2. Persistent organic pollutants — dioxins and furans in food and soil {17 toxic congeners}
3. Microbial toxins — microcystins in drinking water source {90+ variants}

Levels of complexity of analytes

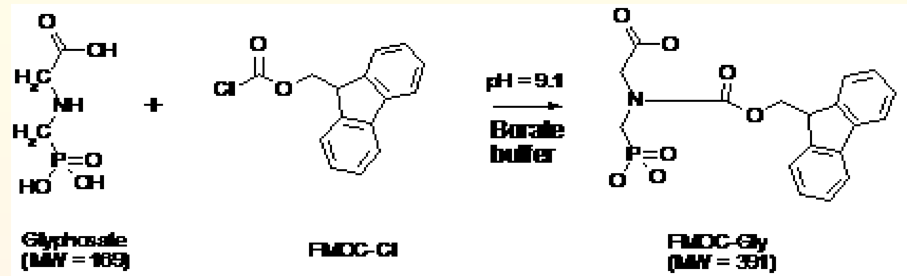
Analyte	Chemical Structure	M.W.
Glyphosate {1}		169.07 g/mole
Dioxins {17}		Dioxins 218-460 Furans 202-444
Microcystins {90+}		900–1100 Daltons

Glyphosate in Drinking Water

Glyphosate Determination – LC-MS Challenges

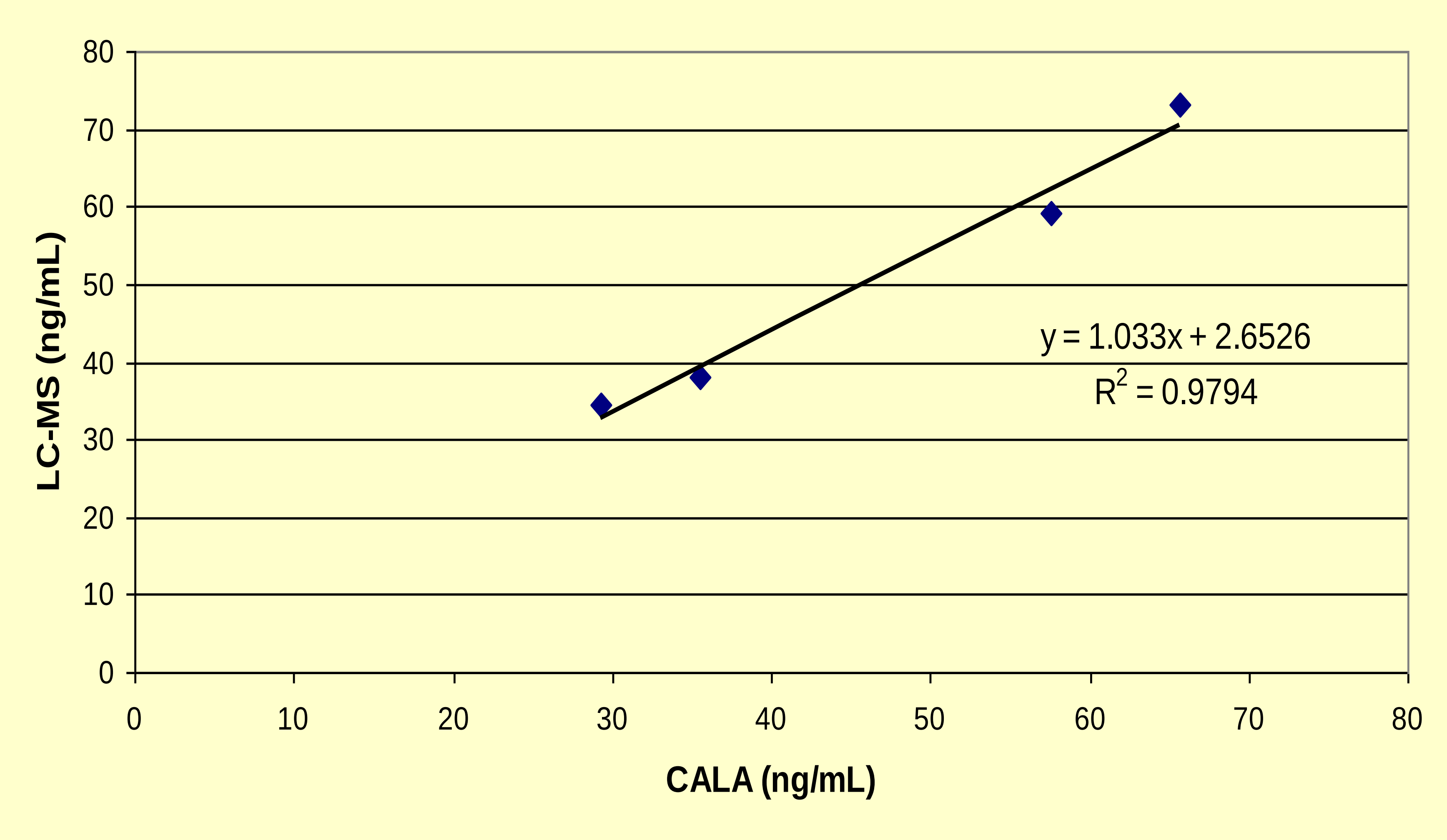
Complex method includes

- derivatization step:

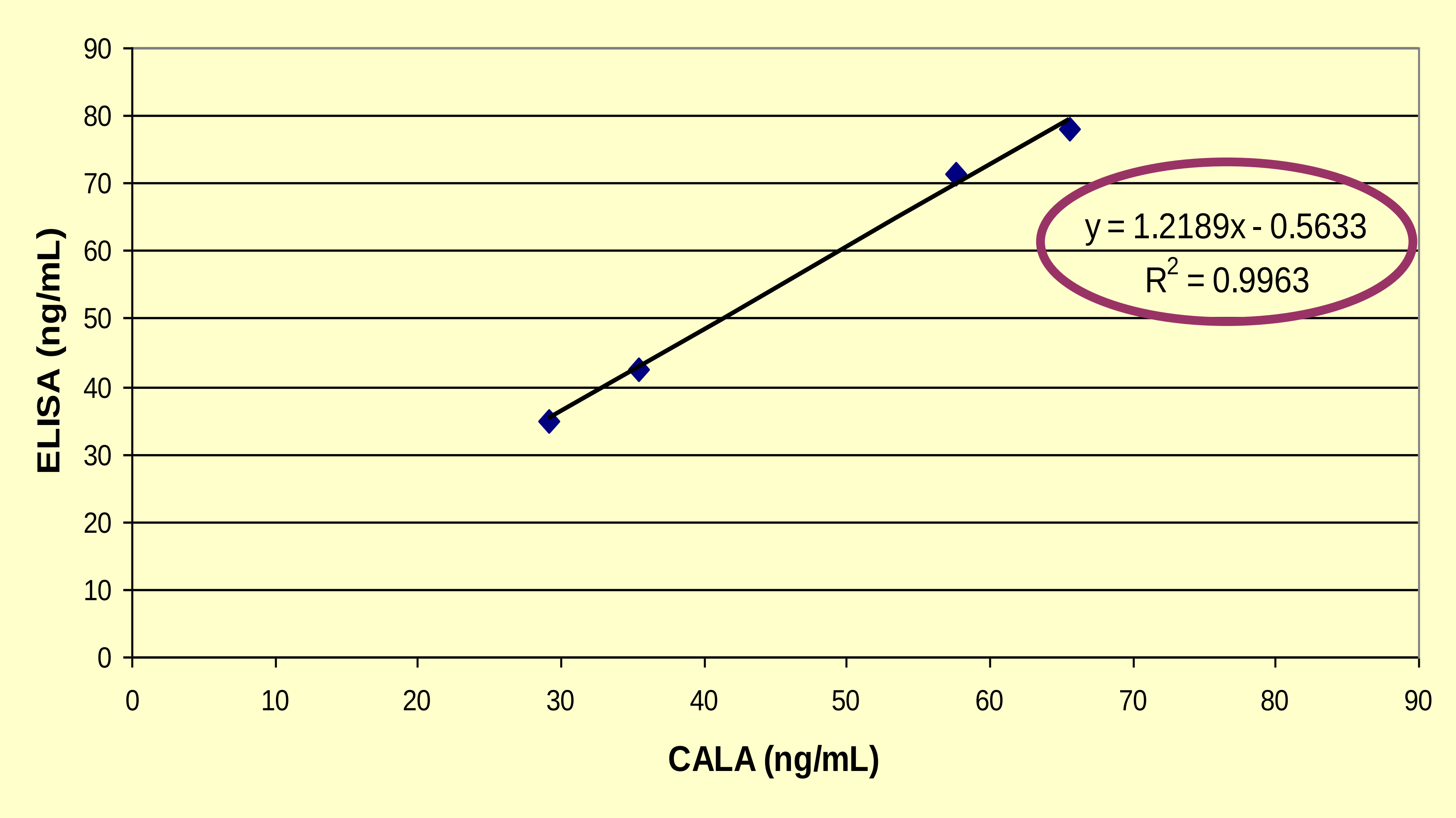


- LC-MS detection:

Proficiency QC Samples: LC-MS vs. CALA



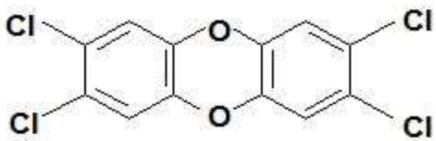
Proficiency QC Samples: ELISA vs. CALA



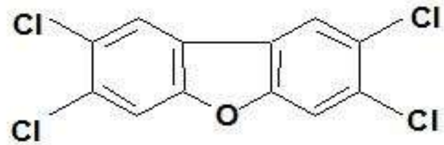
Glyphosate Determination – ELISA Solutions

- ELISA can handle 35 samples per day; LC-MS is about 400 samples per year
- 95% (481/505) drinking water samples in 2007 using LC-MS were glyphosate-negative; elimination of 481 negative samples from LC-MS will save $$$

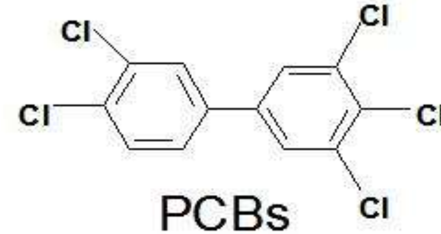
Dioxins / Furans



PCDDs



PCDFs



PCBs

- Likely carcinogens
- endocrine disruption
- autoimmune susceptibility
- wasting syndrome
- Chloracne
- reproductive system changes

GC-HRMS versus ELISA

$150/sample; 209 samples in 11 days

$2,000/sample; 209 samples in 8 months

Gas Chromatography – High Resolution Mass Spectrometry (GC-HRMS)

Enzyme-Linked Immunosorbent Assay (ELISA)

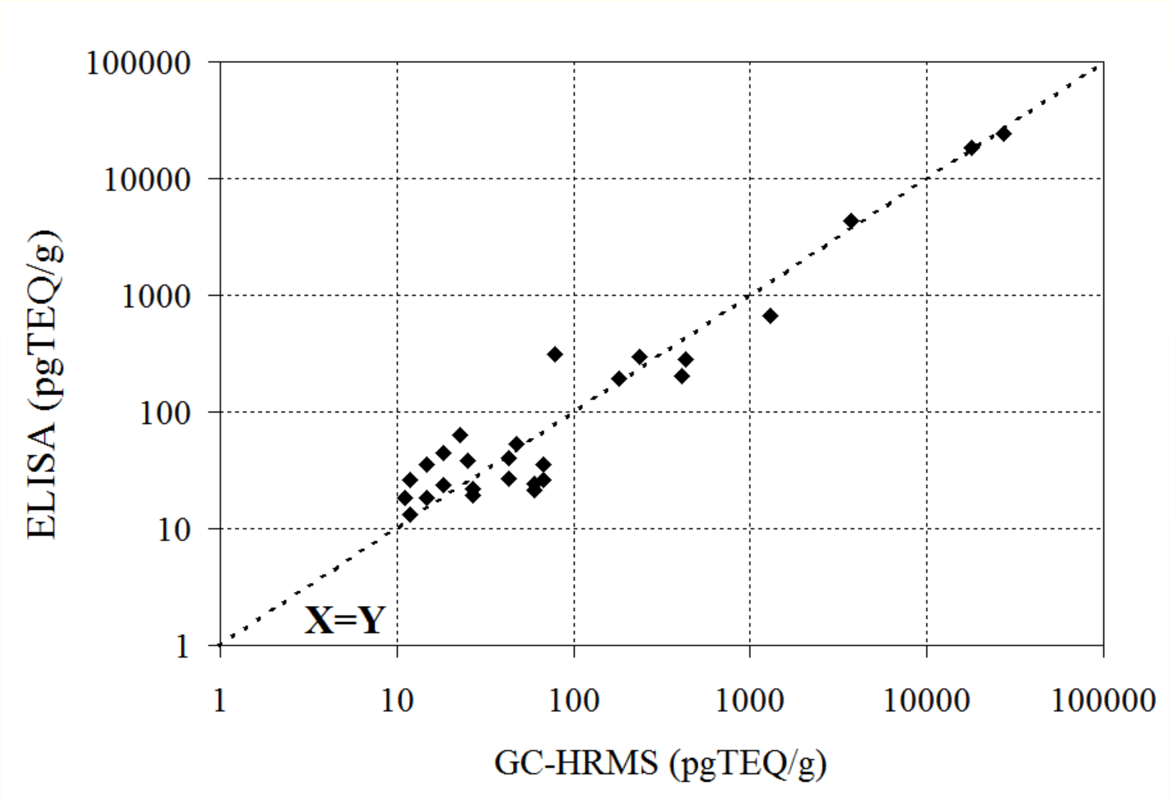
Cost savings by Dioxin ELISA

Table: Annual analytical capacity and cost

Parameter	GC-HRMS	ELISA
# of samples	311	697
Cost	$590,900	$209,100

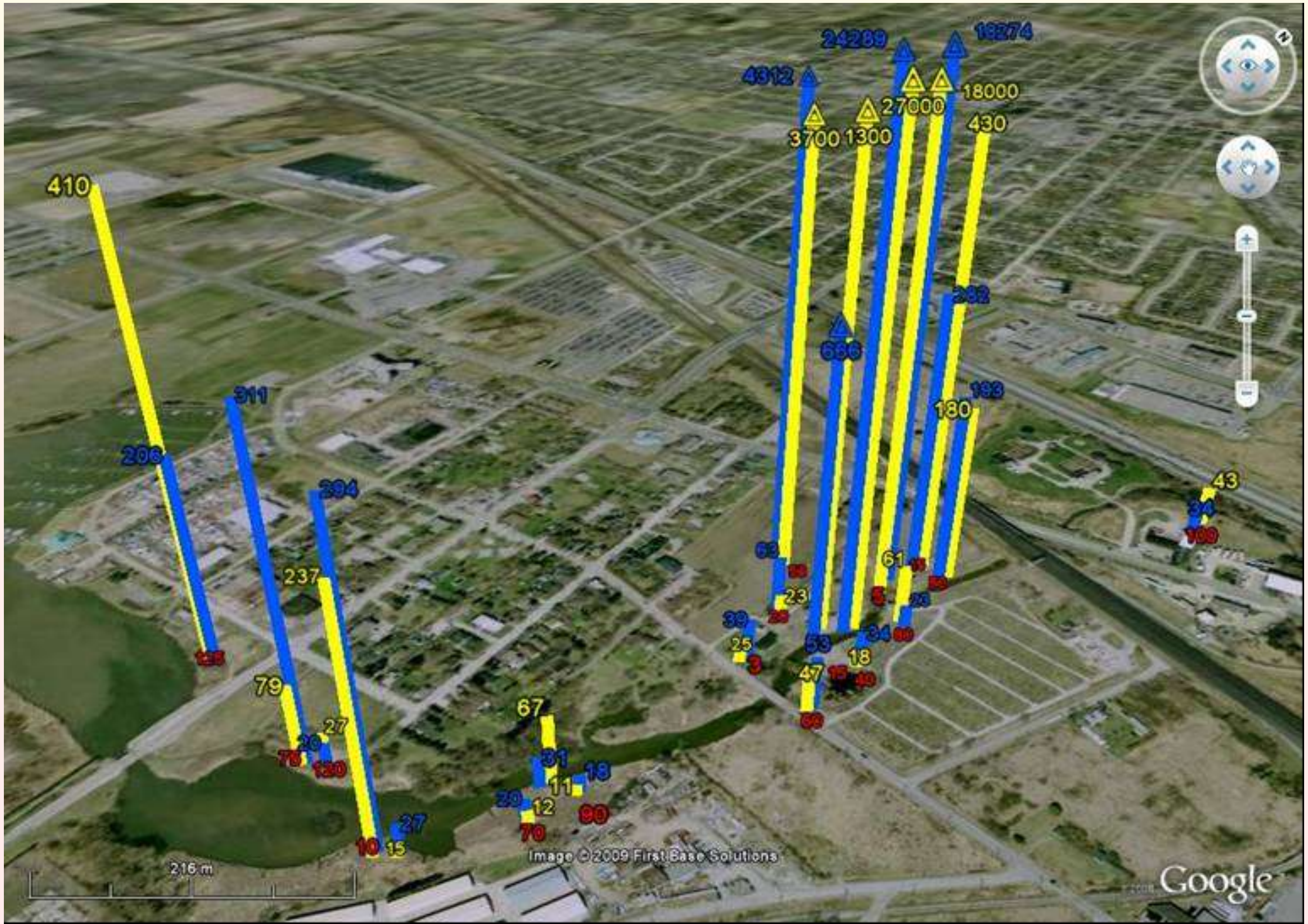
- 2006: 50% of fish samples dioxin-negative

Correlation between ELISA & GC-HRMS

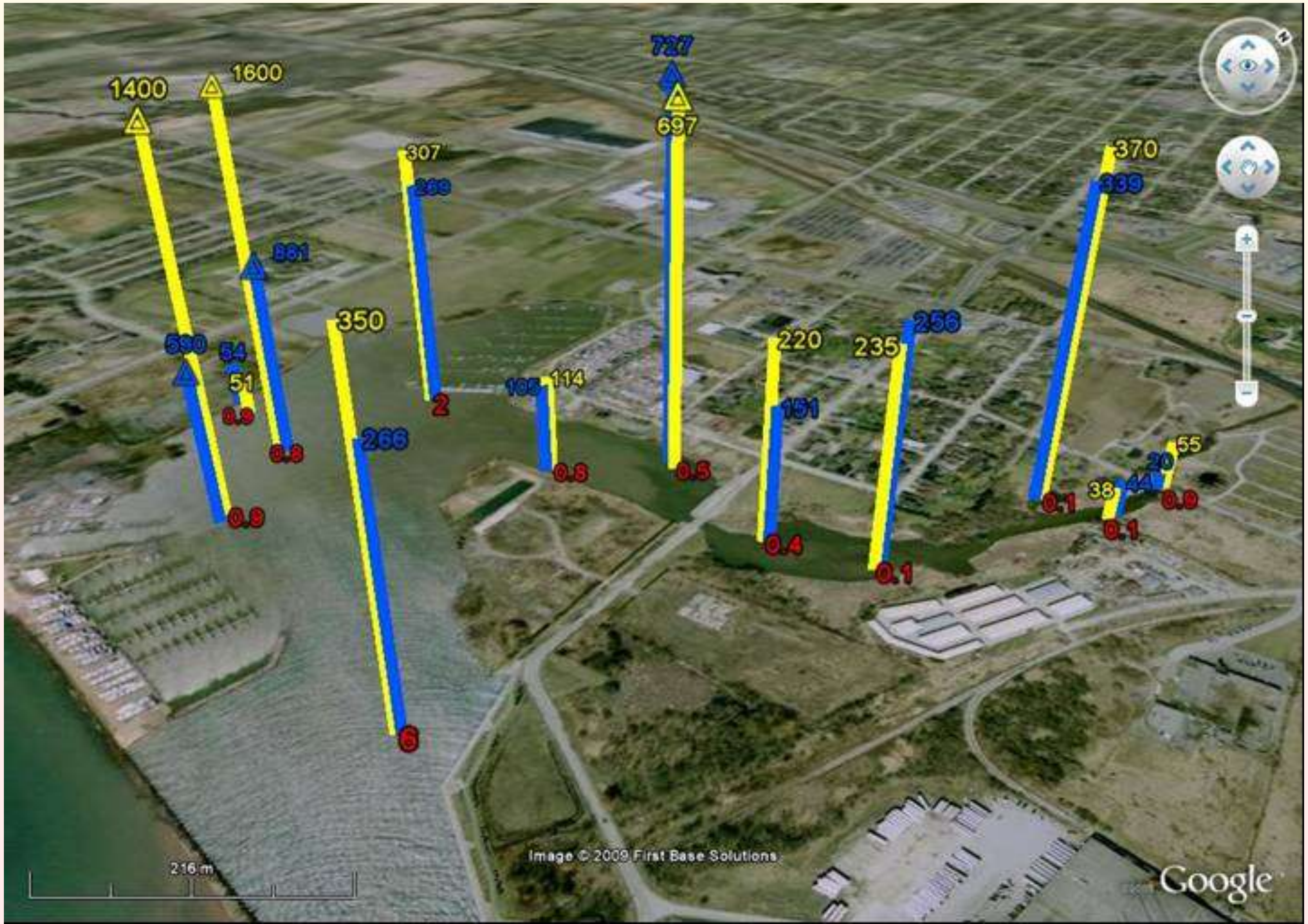


- 27 Soil samples between 11 and 27,000 pgTEQ g^{-1}.
- r^2 = 0.995, slope = 0.94

Upstream aerial map of the test site with an overlay of the soil depths in cm (red), ELISA results in pgTEQ g-1 (blue) and GC-HRMS results in pgTEQ g-1 (yellow)



Downstream aerial map of the test site with an overlay of the sediment depths in m (red), ELISA results in pgTEQ g-1 (blue) and GC-HRMS results in pgTEQ g-1 (yellow)



Cyanobacterial Toxins
(Blue-Green Algae)

Cyanobacteria Bloom Sep 4, 2009: southern tip of Pelee Island, Ontario, Canada border USA; view from aircraft

Impact drinking
water source

October 09, 2008
EMMA REILLY
THE HAMILTON SPECTATOR

Lake Okeechobee, Florida

Blooms Like It Hot

Science Vol. 320, 4 April 2008 pp. 57-58

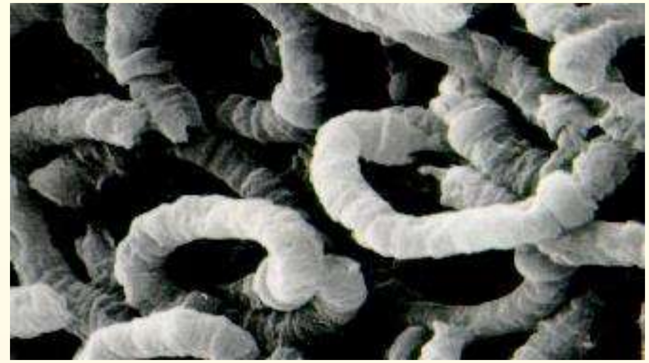
Hans W. Paerl and Jef Huisman

CLIMATE CHANGE

- "…Rising temperatures favour cyanobacteria in several ways. Cyanobacteria generally grow better at higher temperatures (often above 25°C) than do other phytoplankton species such as diatoms and green algae. This gives cyanobacteria a competitive advantage at elevated temperatures…"

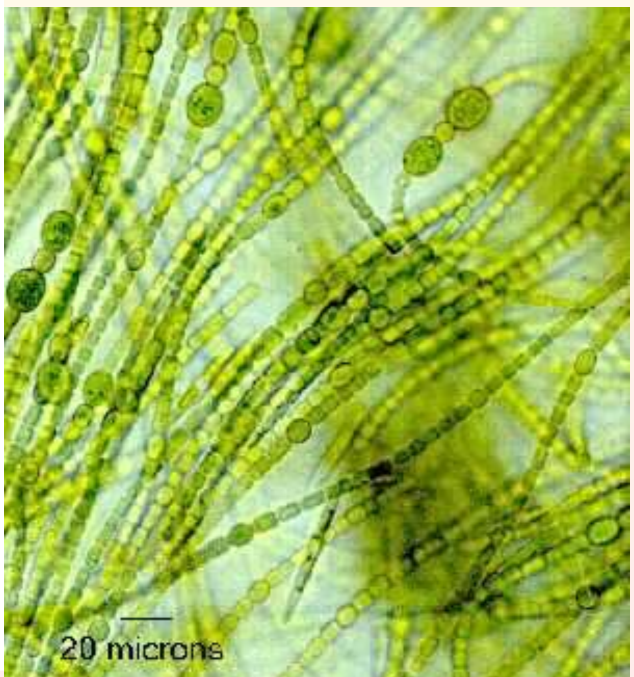
Toxic cyanobacterial genus

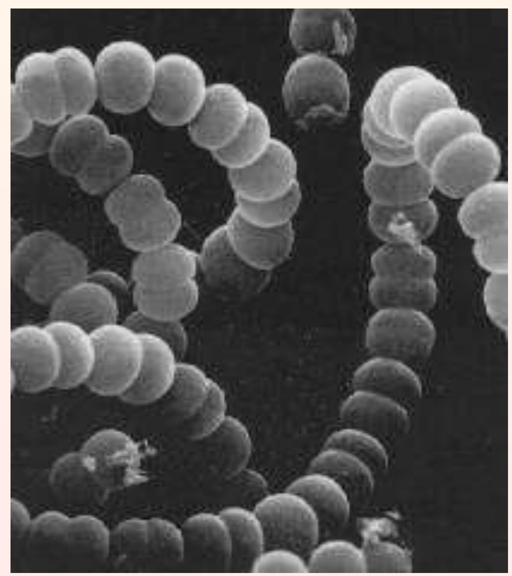
Microcystis aeruginosa



Nodularia spumigena

Oscillatoria

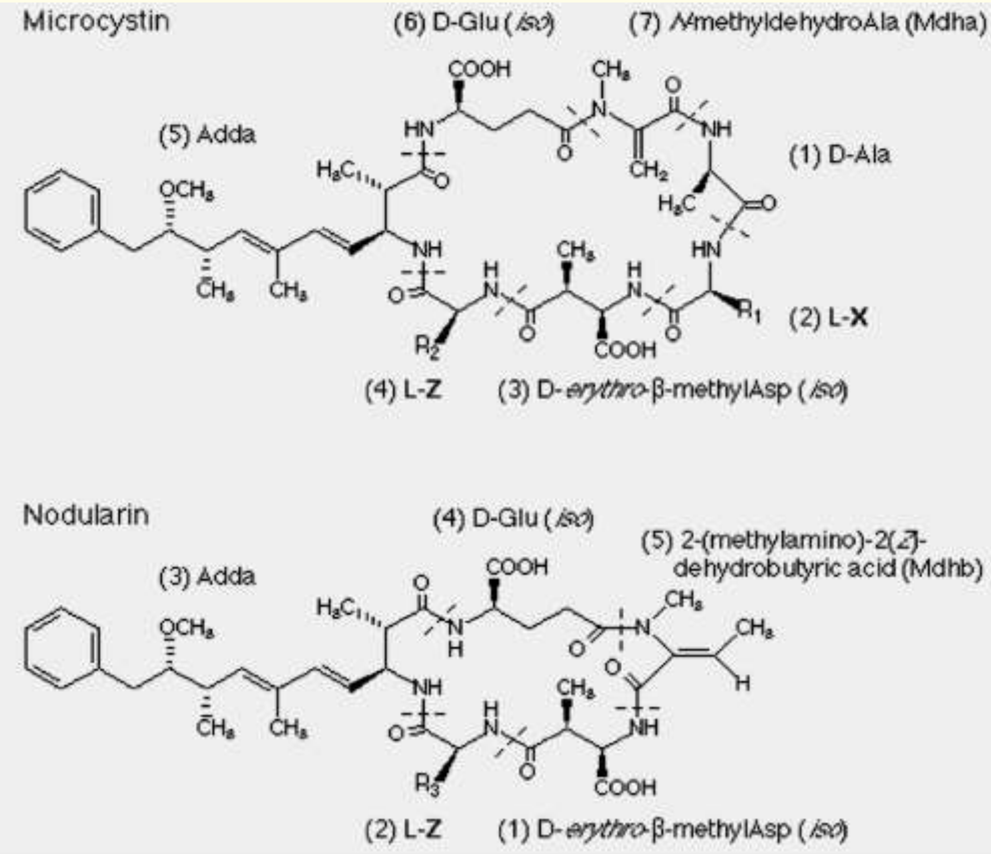




Nostoc

Anabaena flos-aquae

Chemical Structures of Microcystin (over 90) Variants



Cyanobacterial Toxin	L-X Position	L-Z Position
Microcystin-LR	Leu	Arg
Microcystin-RR	Arg	Arg
Microcystin-YR	Tyr	Arg
Microcystin-LA	Leu	Ala
Microcystin-LW	Leu	Trp
Microcystin-LF	Leu	Phe
Nodularin	-	Arg

"The toxic moiety" ADDA (3-amino-9-methoxy-2,6,8-trimethyl-10-phenyldeca-4,6-dienoic acid) is present in > 80% of known toxin variants

LC-(ESI)MS/MS vs. ELISA

$500,000

$7,000

Conclusion: ELISA Usage

Capability	**Report**	**Example**
Quantitative	µg/L (ppb)	**Glyphosate** pesticide
Semi-quantitative	Bioassay Equivalence (BEQ) vs. Toxicity Equivalency (TEQ); (ppt)	**Dioxins** persistent organic pollutant
Qualitative	Presence/absence at threshold of drinking water guideline (ppb)	**Microcystins** bacterial toxin