The Search For Zero: How Low Can We Go and What Does It Mean?

Connaught Summer Institute Presentation

Ray Clement, President, EnviroAnalysis
Nottawasaga Inn, Wednesday, July 20, 2016
Summary

- Analytical testing: why should you care?
- How do you know you’re right? Quality Control!
- Examples from the real world:
  - determination of chlorinated dioxins
  - how low is low?
  - sources of error
Last co-op
work report,
R.E.
Clement
First Benchtop Mass Spectrometer
Deadliest poison found in lake’s fish

Continued from page 1

A very small discovery and it is more than 100 years old. But we will follow it up as fast as we can.

Last week, after warnings about the worsening quality of water in Lake Ontario, provincial and municipal officials said the 200 million gallons that Metro angeles daily from the lake have shown no serious signs of dangerous poisons. The water is likely to remain safe for decades. If not.

John Haltom, Ontario environment minister, said today. “The disease is being treated by the federal government. It is not finding favor in the water where it could be drawn into the public drinking water system.”

Yesterday’s announcement of the discovery of dioxin in lake fish came from New York state health officials.

Marcel Sehler, state health department spokesmen, warned people to exercise extreme caution in eating fish from Lake Ontario and said pregnant women, nursing mothers and children should not eat the fish at all. An advisory against eating the fish has been in effect since 1976 when traces of two toxic chemicals, DDT and PCBs, were found in tested fish.

Flies’ said “trace amounts” of dioxin were found but the ministry is concerned because it represents a “significant pollution.” in the lake’s fish. He said the amount was “scientifically non-hazardous.”

“Conduct analysis”

He said the ministry will conduct “emergency analysis” of fish samples from Lakes Ontario and Erie.

The dioxin, discovered in tests at the University of Nebraska, measured 4.5 parts per trillion in a brown trout caught off Rochester and 4.6 parts per million in a fish caught in the Salmon River estuary at the east end of the lake. The fish were caught in 1977 and 1979 and stored for 10 years. The fish from the Niagara River showed no traces of the chemical.

Dioxin is 500 times more potent than strychnine. A single drop will kill a human. When four pounds of dioxin exploded into the air at a plant in Italy in 1976, hundreds of residents were permanently scarred or otherwise affected the area abandoned.

The source of the dioxin is unknown.

Yalser said. Dioxin is found in tiny amounts in the herbicide 2,4-D, which is heavily used in agriculture and is being released into the Great Lakes until its pollution.

An estimated 300 pounds of dioxin has also been discovered in an abandoned Holter Chemical Co. waste chemical dump at Bloody Run Creek in Niagara Falls, N.Y. It is not known whether the

Yesterday, organizers of the third annual Esquire State Lake Ontario Trout and Salmon Derby, which starts tomorrow, said in Rochester the dioxin discovery wouldn’t hurt the tournament.

“They won’t be deterred.”” People are going to fish anyway,” said Dan Sehler, who sponsored the four-day event, with his wife, Richard.

“They won’t be deterred.”

Mr. Sehler said organizers may post signs to inform entrants of the dioxin danger, but added it likely occurred “the people involved in this are already familiar with the problem.”

As of yesterday, 4,800 people had registered for the derby and a chance to win the $3,000 grand prize and an Evinrude boat motor for the largest brown or lake trout or salmon.

The Star-sponsored Great salmon Hunt, with at least $30,000 in prizes, runs Aug. 18 and runs in Sept.
Number of Dioxin & Furan Compounds

<table>
<thead>
<tr>
<th>Number of Chlorines</th>
<th>Dibenzo-p-dioxin</th>
<th>Dibenzo furan</th>
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<tbody>
<tr>
<td>1</td>
<td>2</td>
<td>4</td>
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<td>1</td>
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<tr>
<td>Total</td>
<td>75</td>
<td>135</td>
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Dioxin Toxicity

NOEL = 3g / kg

LD_{50} = 1ug / kg
Each Molecule has Fingerprint: Mass Spectrum of TCDD
Steps in Analytical Testing

- Clear statement of objectives
- Representative sampling
- Isolation of target compounds (analytes) from all other sample components
- Quantitative measurement of analytes by use of an appropriate detector
- Evaluate results with respect to objectives
Finnigan 4500 GC-MS System
The Limits of Trace Analysis: Detection of 2,3,7,8-TCDD Molecules

<table>
<thead>
<tr>
<th>Weight (Grams)</th>
<th>Number of Molecules</th>
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<tbody>
<tr>
<td>Nanogram (10^{-9})</td>
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</tr>
<tr>
<td>Picogram (10^{-12})</td>
<td>2,000,000,000</td>
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<tr>
<td>Femtogram (10^{-15})</td>
<td>2,000,000</td>
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<tr>
<td>Attogram (10^{-18})</td>
<td>2,000</td>
</tr>
<tr>
<td>Zeptogram (10^{-21})</td>
<td>2</td>
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Accurate or Precise?
Examples of Two Types of Cleanup Columns for Dioxin Analysis
How Do We Know We’re Right?

- **Quality Control: Sampling**
  - sampling containers
  - field blanks
  - replicate samples
  - sample transport and storage (refrigerated)
  - legal samples: chain-of-custody

- **Quality Control: Analysis**
  - method blank
  - internal standard spikes
  - replicate samples
  - instrument calibration & control charts
  - Certified Reference Materials

- **Quality Control: Other**
  - certification and accreditation (ISO, CALA)
  - Inter-laboratory and round-robin studies
  - Standard Operating Procedures (SOPs)
  - Quality Management Unit
  - documentation & continuous training
Data Interpretation: Public Understanding

- Analysis of dioxin in lake water
- 3 samples on consecutive days
- Detection limits 0.1 – 0.3 ppt
- Actual results:
  - Day 1 – 0.2 ppt
  - Day 2 – 0.4 ppt
  - Day 3 – not detected
- What was the newspaper headline?
Levels of dioxin in water double, then disappear

A test last January of Windsor drinking water by the Ministry of the Environment has discovered further traces of dioxin, although subsequent samplings have given the water supply a clean bill of health.

In a test conducted Jan. 21, the ministry found a level of octadioxin of 46 parts per quadrillion (ppq), a figure there are no immediate plans to test for Windsor sources of the chemical, he said.

No traces of dioxin were found in Jan. 21 samples from seven other communities — Hamilton, Sarnia, Amherstburg, Mitchell Bay, Stoney Point, Wallaceburg and Walpole Island. In past tests, minute traces of dioxin were
PUF/Filter Extract Sample
Chromatograms - HxCDD

Lab 6 - 600 pg
PUF/Filter Extract Sample Chromatograms - HxCDD

Lab 3 - ND (48 pg)

Ion 390.00 amu from 11my0501005.d

Abundance

1400
1200
1000
800
600
400
200
0

Time (min.)

17.2
17.6
18.0
18.4

Ion 392.00 amu from 11my0501005.d

Abundance

1000
800
600
400
200
0

Time (min.)

17.2
17.6
18.0
18.4
AIR ROUND-ROBIN: $P_5$ CDFs

LAB A

LAB B

LAB C

1,2,3,7,8-$P_5$ CDF
2,3,4,7,8-$P_5$ CDF
Questions to Ask About Environmental Data

- How have you ensured the sample is representative?
- Were appropriate sample containers used? How were they transported to the laboratory and stored before analysis?
- Were analyses started before the maximum allowable holding time?
- Were chain-of-custody protocols followed?
- Were reported data within the known “Figures of Merit” for method?
- How were detection limits calculated?
- Was detection system used appropriate for target analytes? How was calibration & standardization done, and how often?
- What were knowledge/skill levels of analysts?
- What were results of all blanks?
- Was internal or external standardization used?
MOE’s GC-QqQq-FTMS
3800 GC-320 MS-
920 FTMS
9.4 T Superconducting Magnet
Diesel 1:1000 in MeOH + 0.2% formic acid

Analysis of diesel fuel sample
Analysis of diesel fuel sample

$\text{C}_{18}\text{H}_{22}\text{K}^{+1} (0.32 \text{ ppm})$

$\text{C}_{17}\text{H}_{18}\text{O}_2\text{Na}^{+1} (0.00 \text{ ppm})$

$\text{C}_{16}\text{H}_{19}\text{O}_2\text{Na}^{+1} (0.18 \text{ ppm})$

$\text{C}_{15}\text{H}_{18}\text{O}_4\text{Na}^{+1} (0.11 \text{ ppm})$

$\text{C}_{14}\text{H}_{22}\text{O}_4\text{Na}^{+1} (0.14 \text{ ppm})$

$\text{C}_{13}\text{H}_{26}\text{O}_2\text{Na}^{+1} (0.00 \text{ ppm})$

$\text{C}_{18}\text{H}_{22}\text{ONa}^{+1} (0.40 \text{ ppm})$

$\text{C}_{15}\text{H}_{26}\text{O}_3\text{Na}^{+1} (0.28 \text{ ppm})$

$\text{C}_{16}\text{H}_{30}\text{O}_2\text{Na}^{+1} (0.00 \text{ ppm})$

$\text{C}_{17}\text{H}_{34}\text{ONa}^{+1} (0.03 \text{ ppm})$

Mass/Charge

277.00  277.05  277.10  277.15  277.20  277.25  277.30
Analysis of diesel fuel sample

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<th>Data Points</th>
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<td>2048K</td>
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<tr>
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<td>512K</td>
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<td>128K</td>
</tr>
<tr>
<td>1,500</td>
<td>32K</td>
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Toxins fouling our food: Report

By PAULINE COMEAU and TOM GODFREY
Staff Writers

Food is the primary source of dangerous toxins found in Metro residents and will force the Canadian government to re-examine acceptable levels of chemicals, a report released yesterday shows.

The Toronto Sun, Tuesday May 20, 1986

Toxins through food and "things could get worse unless we take the clean-up of the environment more seriously."

"While there is no cause for immediate concern," he said, "we have to take vigorous measures for the future and I would think the results would prompt a second look at a number of areas (of measurement) and the way we look at toxic chemicals in our environment."

The $10,000 study, prepared by Kate Davies, shows residents of Southern Ontario ingest eight times the amount of dangerous toxins, like dioxin, PCBs, and DDT, in food than in water or air.

Dioxin levels in some cases, especially in fruit, were found to be 70 times the limits suggested in a discussion paper of the Ontario Environment Ministry.

Macpherson said last night that most of the country's energy has been used so far to solve the problems of water and air pollution.

But the study shows that water is responsible for only 11% of the toxins ingested by humans, air about 4%, and food 86%.

"We had a good idea from other studies that food would be higher, but the ratio was a little higher than we expected," said Macpherson.

Chemicals were found in milk, eggs, fruits, meat, and vegetables.

Macpherson said the test was conducted on foods bought in several stores throughout Toronto last summer and early this year.

The chemicals work their way into food through several sources — rain, soil, and irrigation by contaminated water, he said.

The levels found in food where levels have been set, were well below the standards set by the government, said Macpherson, but the levels could be expected to increase over the next generation.
WITH ALL THIS DIOXIN, LOOKS LIKE WE’LL BE SAYING OUR PRAYERS AFTER OUR MEAL!
New York
Apples

Ontario
Peaches

Ontario
Potatoes

Western Canada
Wheat
Future of Testing: How Many Chemicals?

Date: Mon May 16, 2005
Count: 25,702,447

Date: Mon May 09, 2016
Count: >111,000,000
Lessons Learned

- Hard Work is More Important than Great Talent
- You Can’t Get What You Want Until You Know What You Want
- It’s not your Aptitude, but your Attitude that determines your Altitude
- You get what you want by helping others get what they want
- Time is more important than money
- Work must have clear objectives
- Importance of teamwork
- Big difference between doing things right and doing the right things
- Technical writing skills & soft skills
- Proactive is better than reactive
- Take care to protect your health!!!
The Greatest Discovery

“The Greatest Discovery Of Any Generation Is That A Human Being Can Alter His Life By Altering His Attitude”

– William James