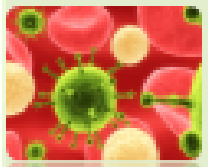
AIR MONITORING AT PIPELINE SPILLS – ADDITIONAL OPTIONS FOR LANDOWNER AND RESIDENT CONCERNS

Why is this important?

- What killed people a few hundred years ago is different from what kills you today.
- Then, the leading causes of death included childbirth, infectious diseases and accident.
- Now, we are seeing significant increases in the prevalence of chronic conditions such as diabetes, autism, cancers, allergies, asthmas and heart disease.



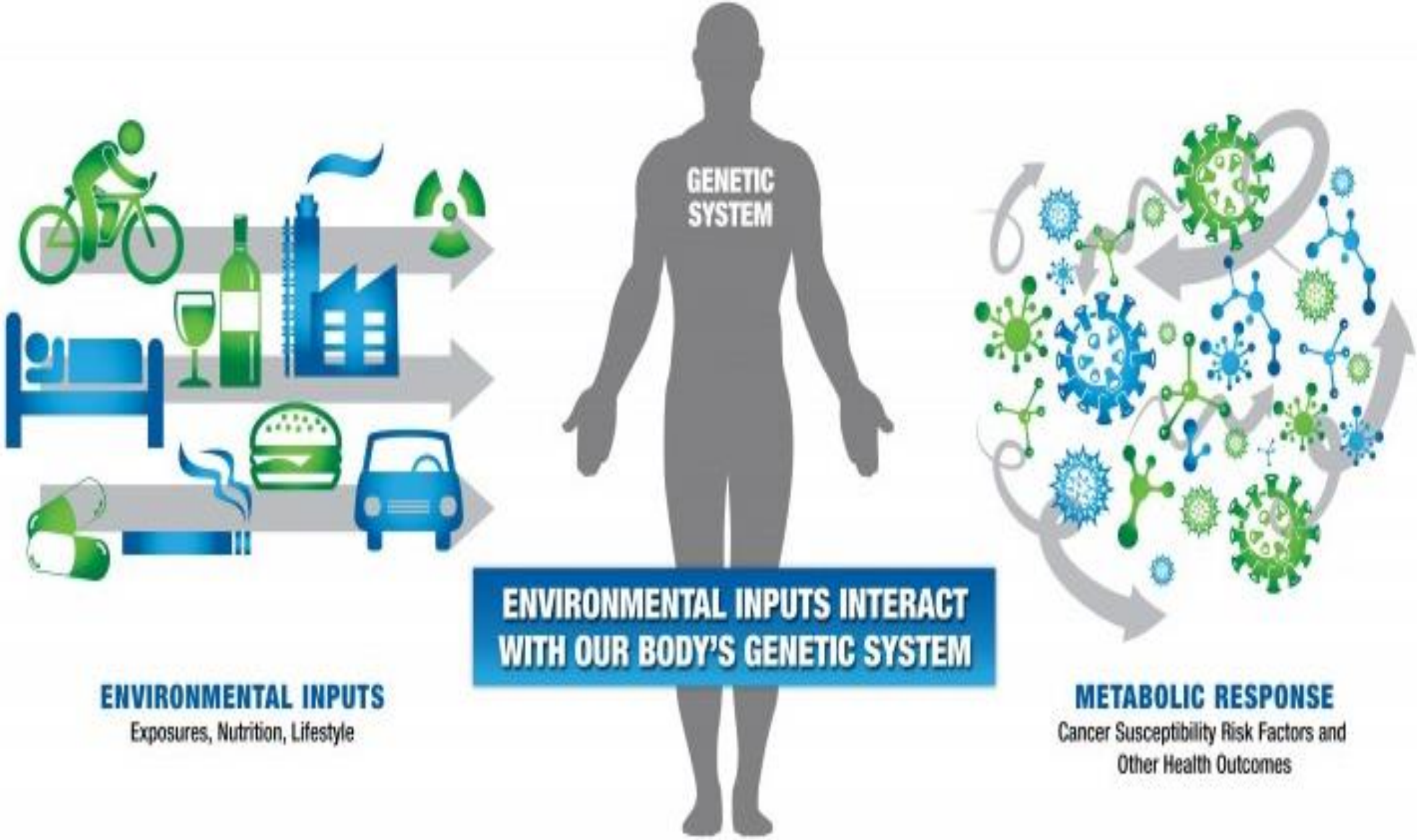

WHAT HAS CHANGED?

Not humans. We have the same genetic makeup that we did as cavemen and genetic changes cannot account for increases in such chronic conditions.

Advancements in public health – Life expectancy and quality of life have been improved by such things as vaccinations, maternal care, better nutrition, drinking water and better basic health care.

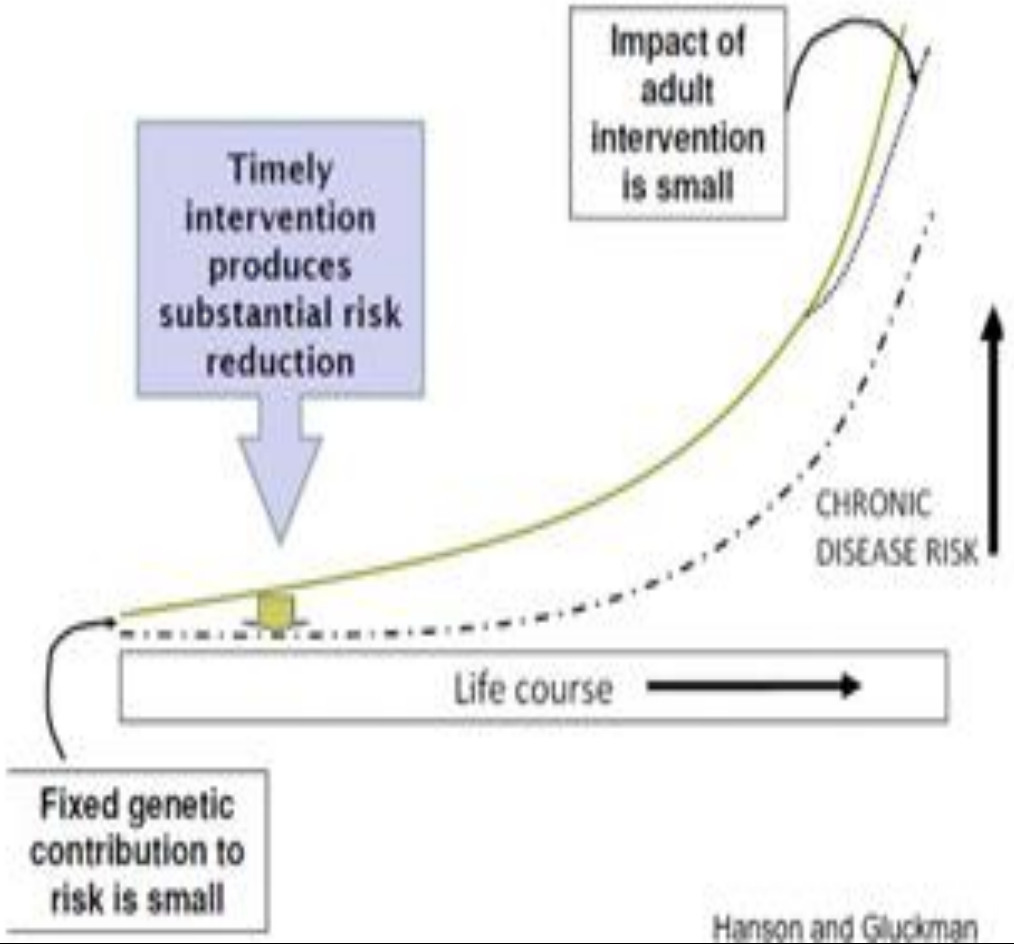
Chemical exposure - Since World War 2 and the invention of plastics, humans are exposed to thousands of new chemicals which are ubiquitous in our daily environment, not to mention pharmaceuticals in our water supply.

Chemical exposures ARE having an effect on humans.

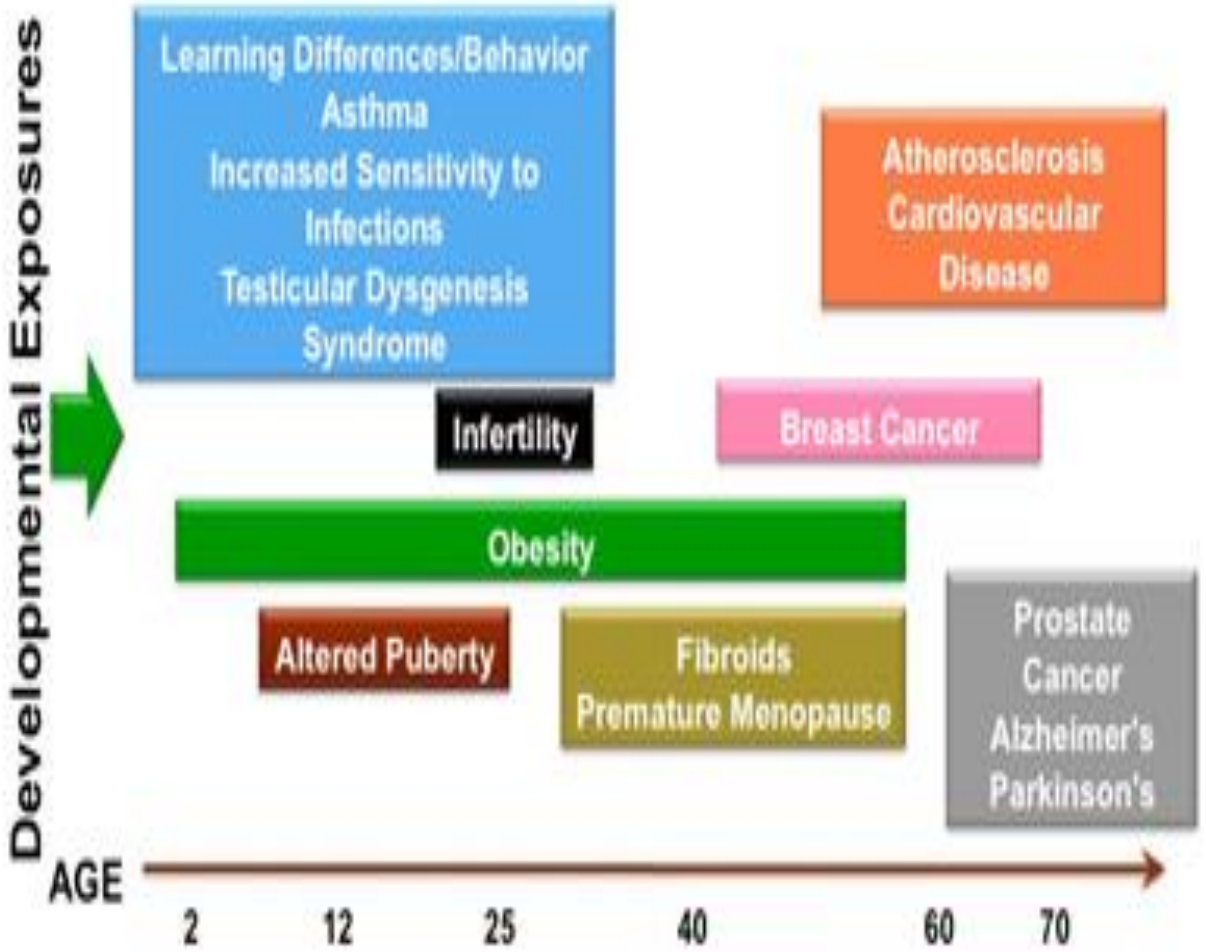

GENETIC SYSTEM
ENVIRONMENTAL INPUTS INTERACT WITH OUR BODY'S GENETIC SYSTEM
ENVIRONMENTAL INPUTS
Exposures, Nutrition, Lifestyle
METABOLIC RESPONSE
Cancer Susceptibility Risk Factors and Other Health Outcomes

(NIH, 2012)

Development is Most Important Time to Intervene to Prevent Disease



Examples of Developmental Origins of Health and Disease (DOHAD)

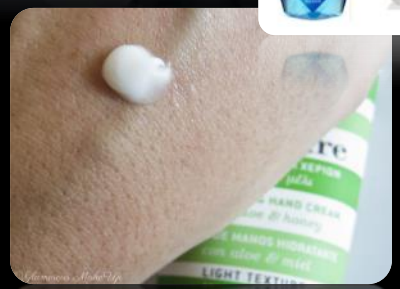


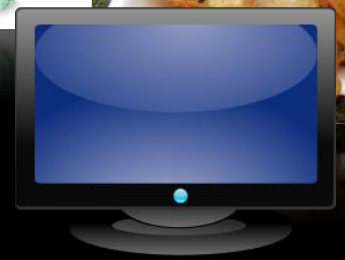
(NIH, 2012)

Toxic Effects
EVERYDAY
EXPOSURES

We often think of our homes as a sanctuary, a place of safety we can go to for rest and relaxation and to recharge for the next day. Home is a place where life happens and where families grow. But did you know that your home is filled with chemicals? Everyday exposures to toxins occur through the products we use each day that make life more convenient. Click through the rooms of the home to see where everyday exposures occur and how you can limit your family's exposure to these dangerous chemicals.

WHAT'S MY POINT?





ADVERSE HEALTH EFFECTS FROM AIR POLLUTION

- One of the most common requests that we get is to evaluate the potential for adverse health effects due to odors generated in the field due to oil and gas operations.
- Ambient air monitoring equipment is adequate for routine monitoring purposes, as are passive filters, but cannot address novel or high-end parameters in terms of detection limits and the limitations to small amounts of potential analytes.

ADVERSE HEALTH EFFECTS FROM AIR POLLUTION

Point source testing using summa canisters, bags, or charcoal tubes is much more accurate, but still requires pre-knowledge of the contaminants of concern in order to test for them.

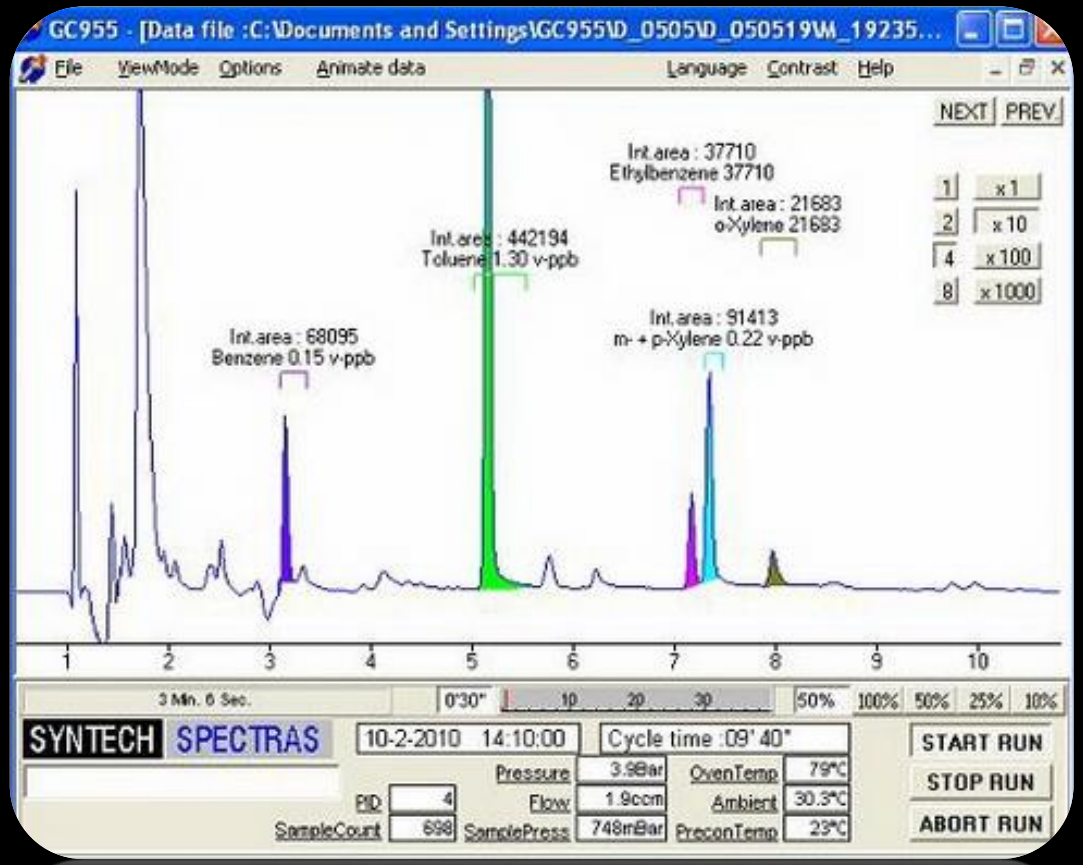
SO WHAT DID WE DO ABOUT IT?

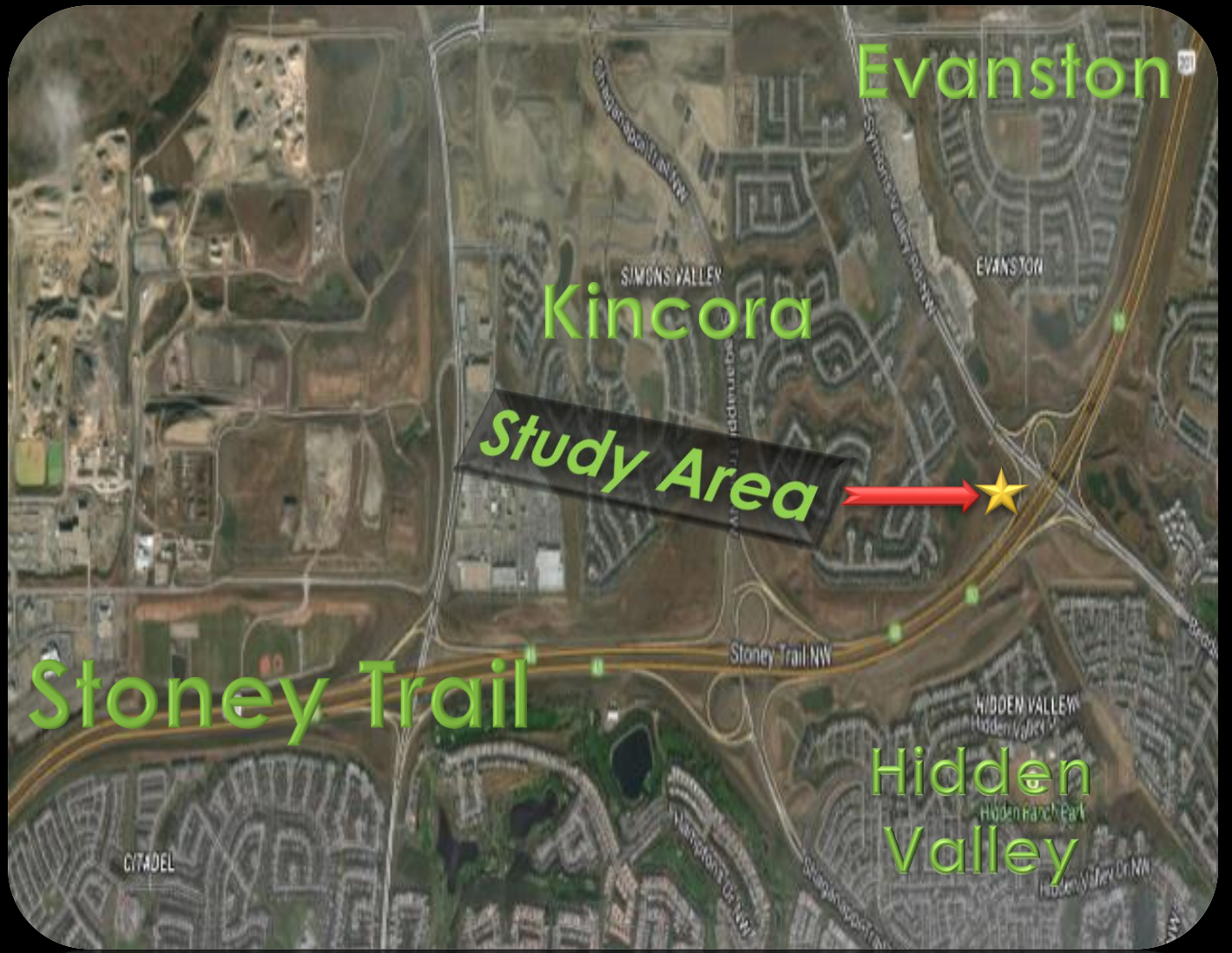
- Summa canisters and charcoal tubes require a technician to sample regularly in field if extended periods of time are required to be monitored.
- An alpha/beta Continuous Air Monitor (iCAM) was used to collect a month's worth of air samples, with no changing of filters required.
- Traditionally, this instrument measures airborne alpha and beta particulate activity with radon/thoron alpha and beta background compensation.
- This has now been used in real world applications as well.

SAMPLING PROTOCOL

- Samples were placed in a ditch of a median on Stoney Trail for a period of 1 month, from mid-September to mid-October, 2014. Note that pesticide levels still persist, despite being the end of the lawn and garden season.
- 4 test monitors were placed on site, to ensure that enough sample was garnered for the extensive list of analytical.
- Samples were checked and collected every week to ensure that they maintained integrity, although this was not strictly required.
- **Air sampling and screening can provide evidence that a problem exists, whereupon conventional testing can be done to pinpoint and address the issue.**

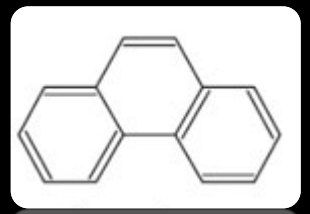
STUDY AREA

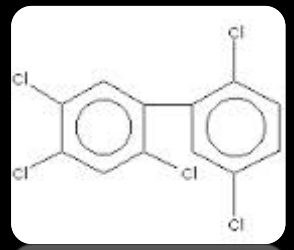

GC955 - [Data file :C:\Documents and Settings\GC955\D_0505\D_050519\M_19235...
File ViewMode Options Animate data Language Contrast Help
NEXT PREV
Int.area : 37710
Ethylbenzene 37710
Int.area : 21683
oXylene 21683
Int.area : 442194
Toluene 1.30 v-ppb
Int.area : 68095
Benzene 0.15 v-ppb
Int.area : 91413
m- + p-Xylene 0.22 v-ppb
1 x1
2 x10
4 x100
8 x1000
1 2 3 4 5 6 7 8 9 10
3 Min. 6 Sec.
0'30"
50% 100% 50% 25% 10%
SYNTECH SPECTRAS
10-2-2010 14:10:00
Cycle time :09' 40"
START RUN
STOP RUN
ABORT RUN
Pressure 3.9Bar
Flow 1.9ccm
SamplePress 748mBar
OvenTemp 79°C
Ambient 30.3°C
PreconTemp 23°C
PID 4
SampleCount 698

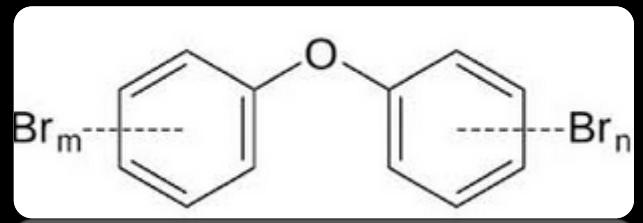

Evanston
Kincora
Study Area
Stoney Trail
Hidden Valley
SIMONS VALLEY
EVANSTON
Stoney Trail NW
HIDDEN VALLEY
CITADEL

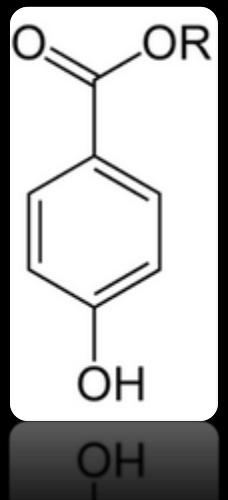
WHAT WE TESTED FOR…

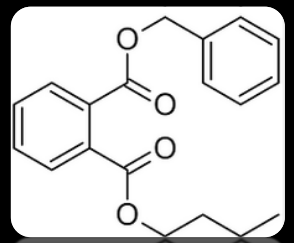
- In place of the fixed, card mounted filter, which must be changed manually at regular intervals, the mechanism passes a continuous belt of filter material under the detector. The filters were collected and run for a number of parameters, including:
- PAHs
- PCBs
- Phthalates
- VOCs
- BTEX F1-F4
- SVOCs
- Metals
- Particle Size
- OC and OP Pesticides





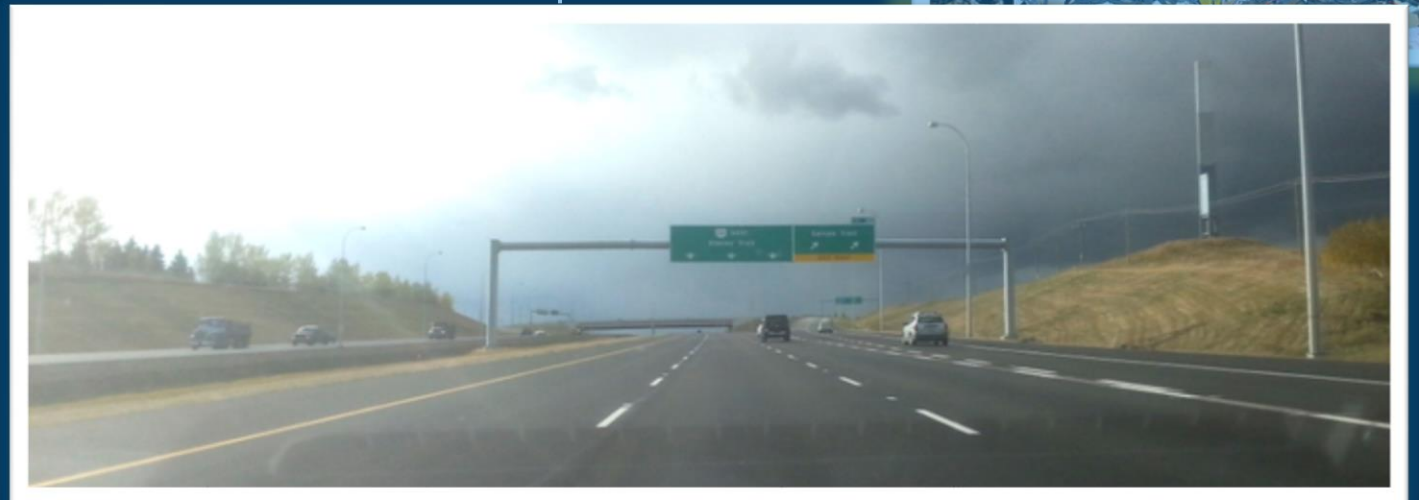






POINT SOURCE TESTING RESULTS

- Elements and compounds of note are listed on the next slide.
- Compounds with values below detection limit are not included.
- Overall, 238 parameters were analyzed.
- Results are summarized to show a yearly intake, based on a conservative proposed one hour of outside exposure a day.



Analyte (ug/L)	YEARLY SUM
Metals	
Aluminum	9453.36
Barium	13293.60
Boron	15317.80
Calcium	16379.59
Iron	1068.47
Magnesium	2020.47
Potassium	11352.35
Sodium	28910.38
Zinc	10164.40
PHCs	
F2 PHCs (C10-C16)	1902.0
F3 PHCs (C16-C34)	1409.4
VOCs	
1,3-Dichlorobenzene	1500.6
1,4-Dichlorobenzene	1502.2
1,2-Dichloroethane	3122.8
SVOCs	
4-Chloro-3-methylphenol	1419.4
Azobenzene	6367.2
Benzo [b] fluoranthene	730.00
Bis(2-chloroethoxy)methane	1054.44
Bis(2-chloroisopropyl)ether	932.78
Bis(2-ethylhexyl)phthalate	1987.2
Dibenzo [a,h] anthracene	202.78
Diethylphthalate	358714
Di-n-butylphthalate	40231
Isophorone	648.89
Nitrobenzene	3001.1
Pesticides	
Atrazine	1404.5
2,4-D	1210.9

This is all well and fine…very scientific…and expensive!
~ $30,000 worth of testing, and so what is it telling me? Will I get sick breathing this air based on these results?

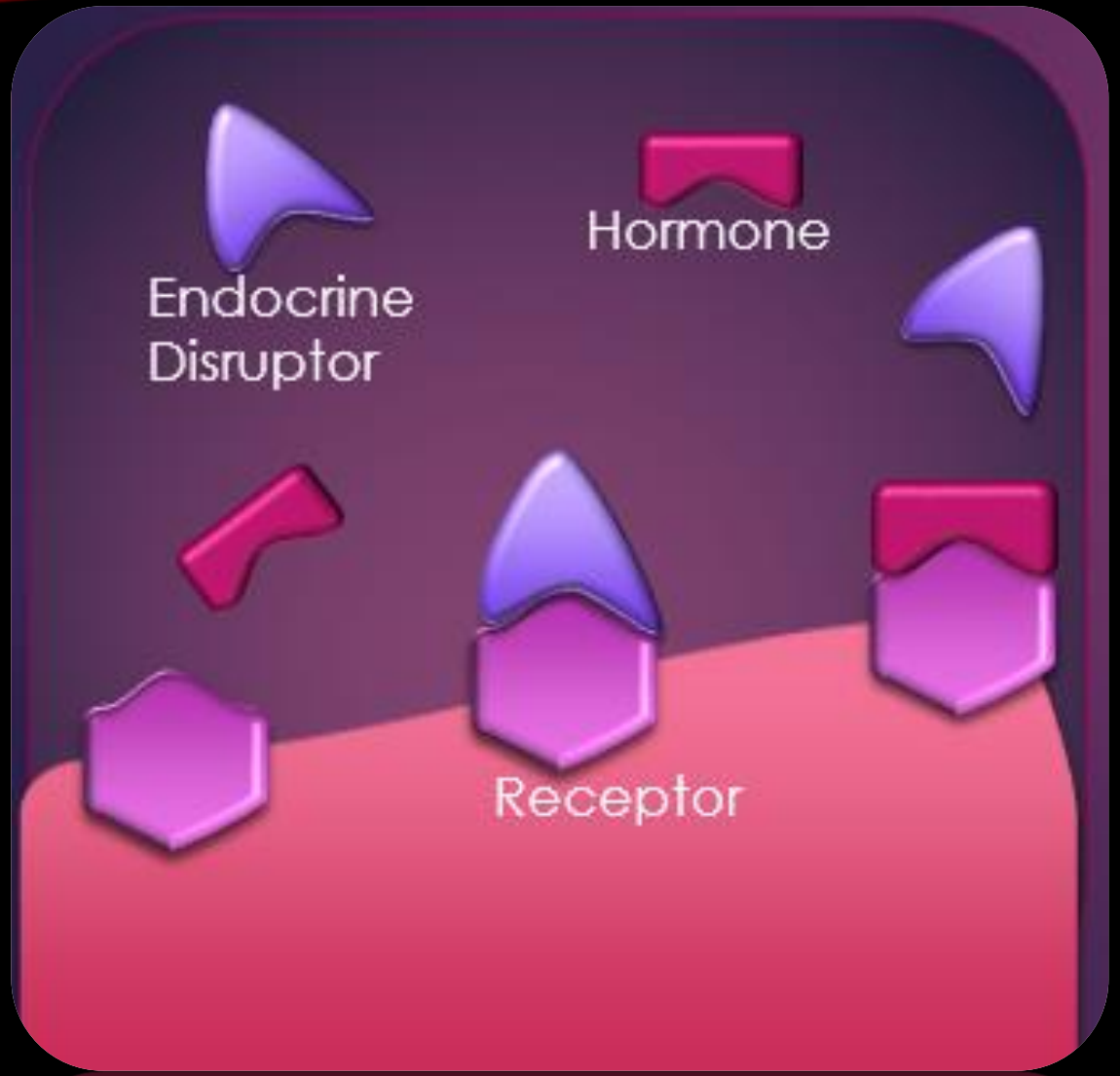
YEAST ESTROGEN ASSAY

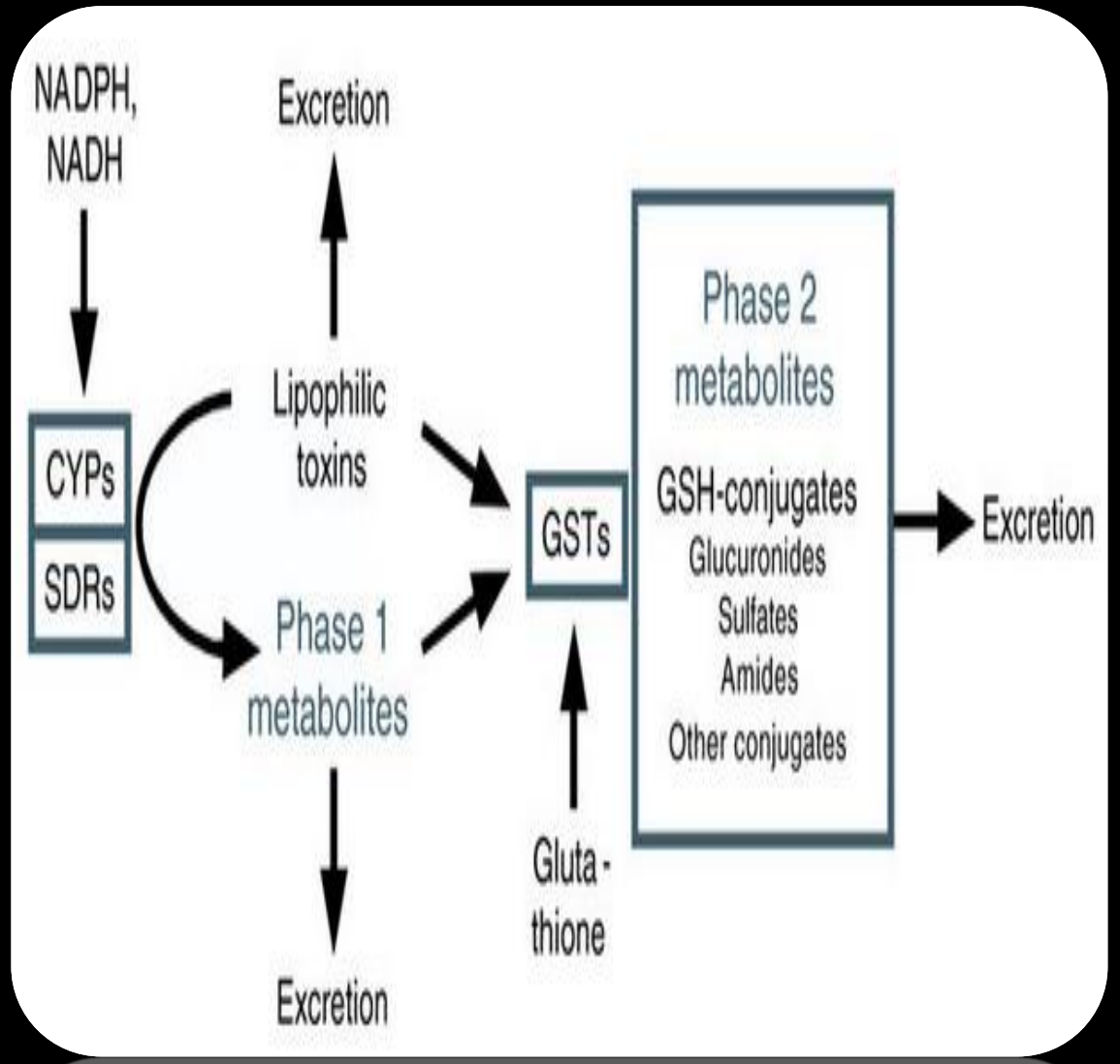
Because point source testing has yielded some results, the question becomes "What of them?" and "Will they cause adverse health effects?"

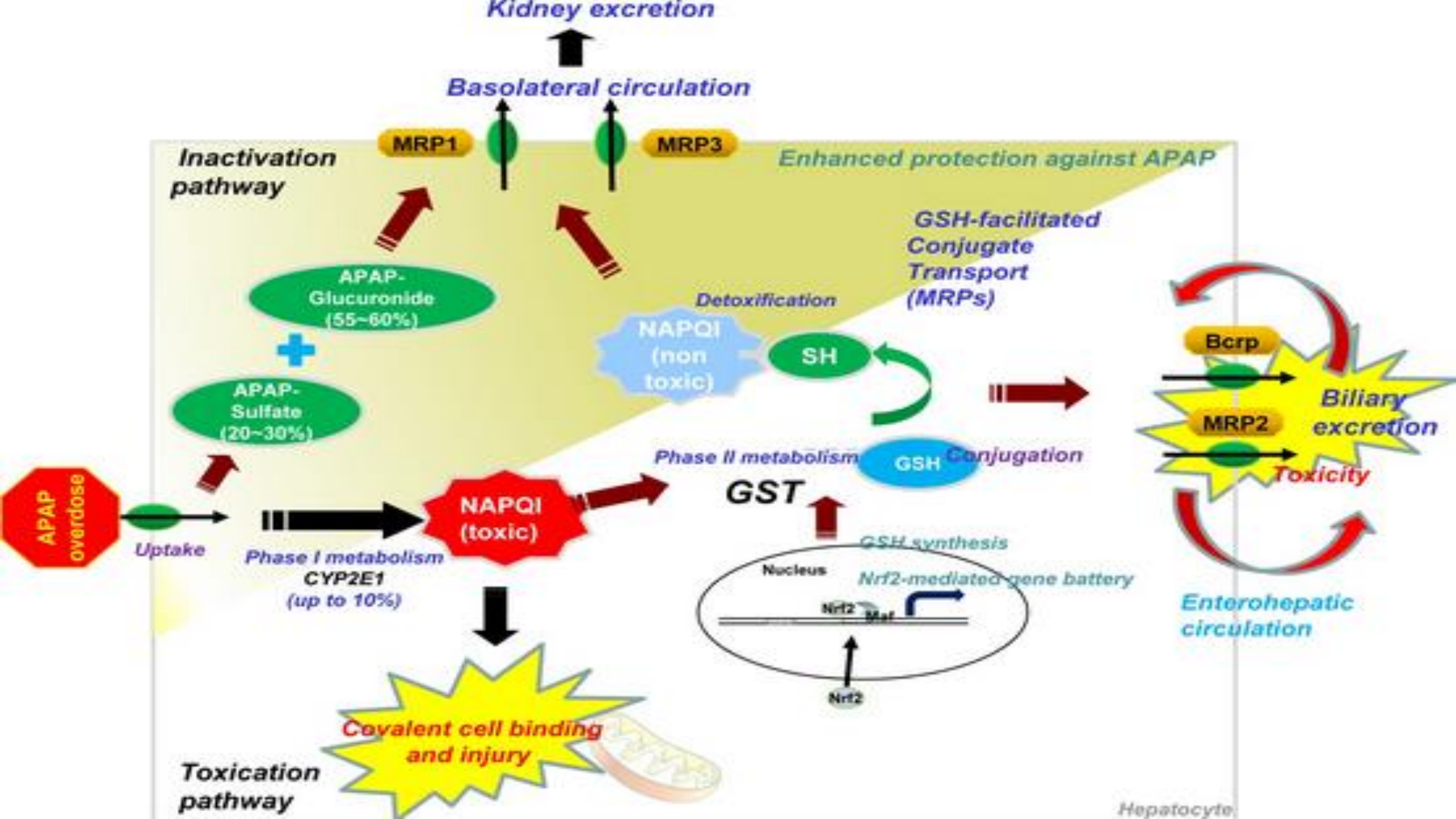
In this case: from doing yeast estrogen assays, the answer is, likely yes – there was a strong estrogenic response to this novel screen and extraction technique that shows that…

There are chemicals of concern that have the capacity to cause adverse health effects in samples that PASS ambient air quality criteria.

MECHANISMS OF ACTION

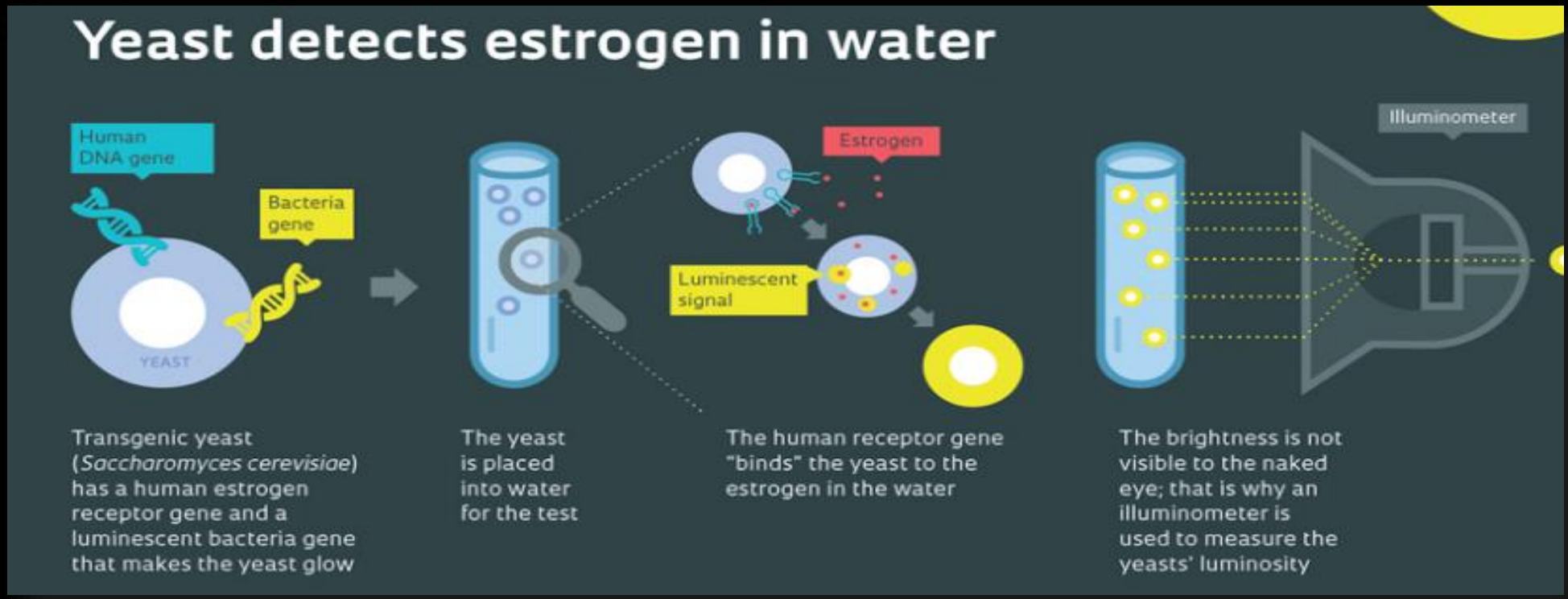




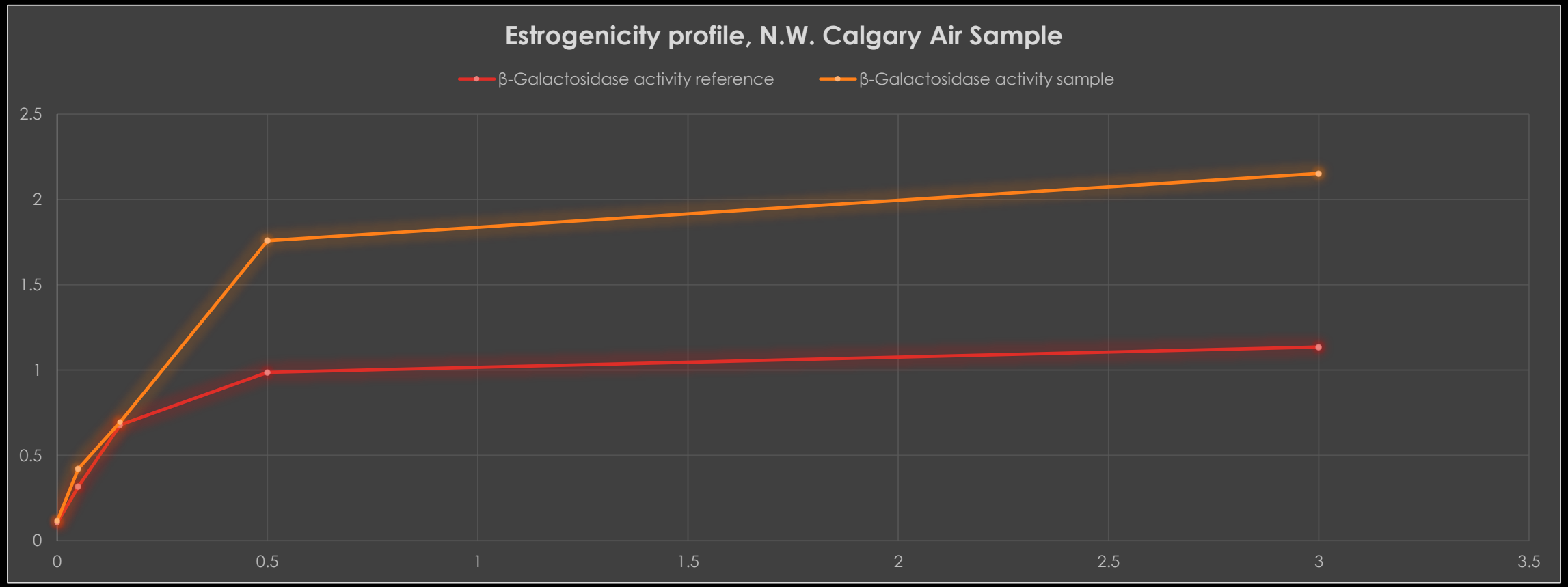

Kidney excretion
Basolateral circulation
MRP1
MRP3
Inactivation pathway
Enhanced protection against APAP
GSH-facilitated Conjugate Transport (MRPs)
APAP-Glucuronide (55~60%)
APAP-Sulfate (20~30%)
Detoxification
NAPQI (non toxic)
SH
Bcrp
MRP2
Biliary excretion
Toxicity
Phase II metabolism
GSH
Conjugation
GST
APAP overdose
Uptake
NAPQI (toxic)
Phase I metabolism
CYP2E1
(up to 10%)
GSH synthesis
Nucleus
Nrf2-mediated gene battery
Nrf2
Maf
Nrf2
Enterohepatic circulation
Covalent cell binding and injury
Toxication pathway
Hepatocyte

ESTROGENIC RESPONSE

- Yeast that has been transfected with the human estrogen receptor (hER) gene as well as expression plasmids that carry an ERE and the reporter gene LacZ that encodes the enzyme X -galactosidase was used to test for estrogenic response potency.
- A positive dose–response curve of 17β –estradiol was used as a reference.

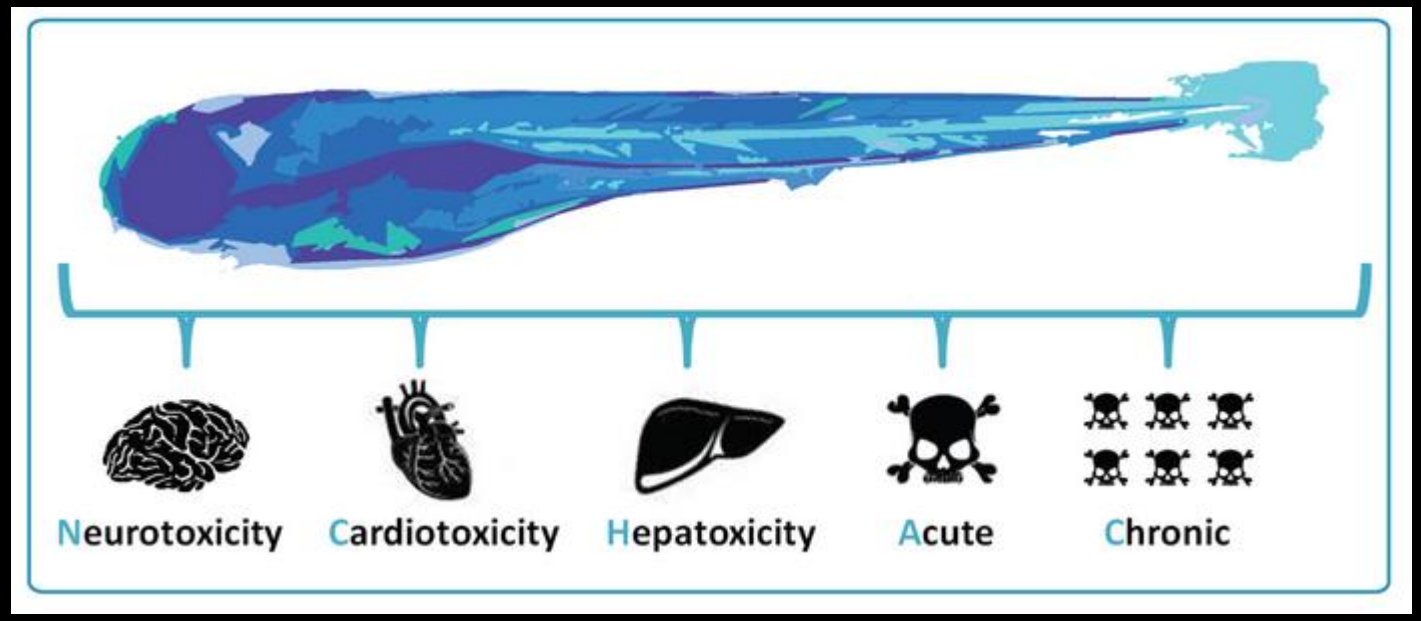


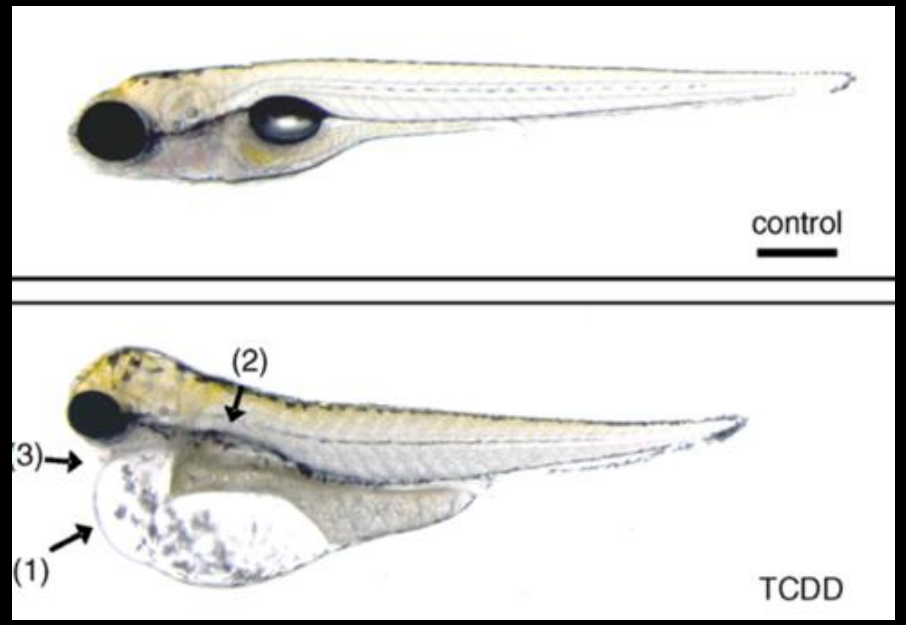
ESTROGENICITY PROFILE



ZEBRA FISH NEUROTOXICITY AND MUTAGENICITY

Further potential steps also exist…

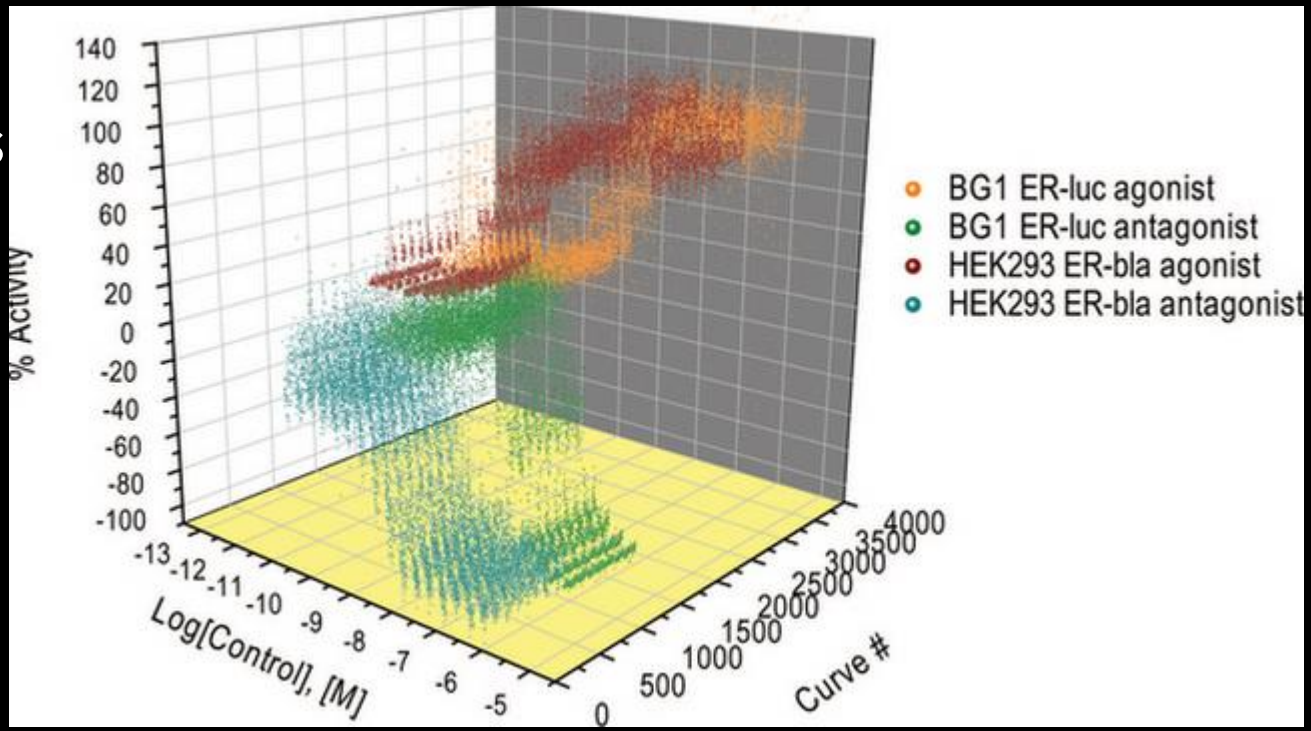




2,3,7,8-Tetrachlorodibenzodioxin

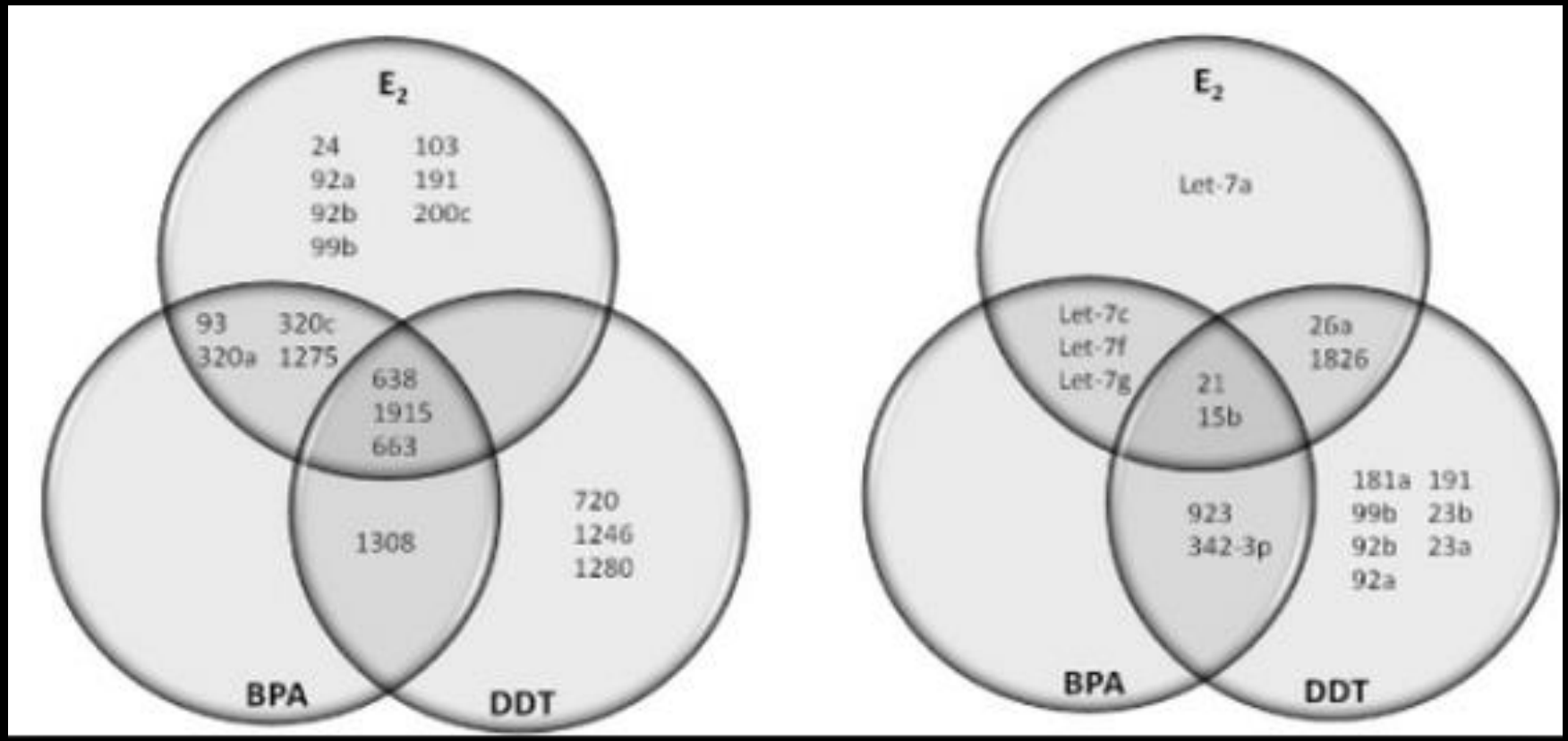
MCF-7 ASSAYS

- Affected proteins regulate oxidative stress - superoxide dismutase and structural proteins such as actin or tropomyosin - may explain morphological changes of cells.
- USEPA has started validation of this protocol
- Improved the process by adding more robust weaker agonist controls.
- Derived from MCF-7 immortalized human breast adenocarcinoma cells and endogenously express both human ERa and Erβ.
- Involve the competition of a given compound with radiolabeled estradiol for specific binding to the ER.



FUTURE WORK

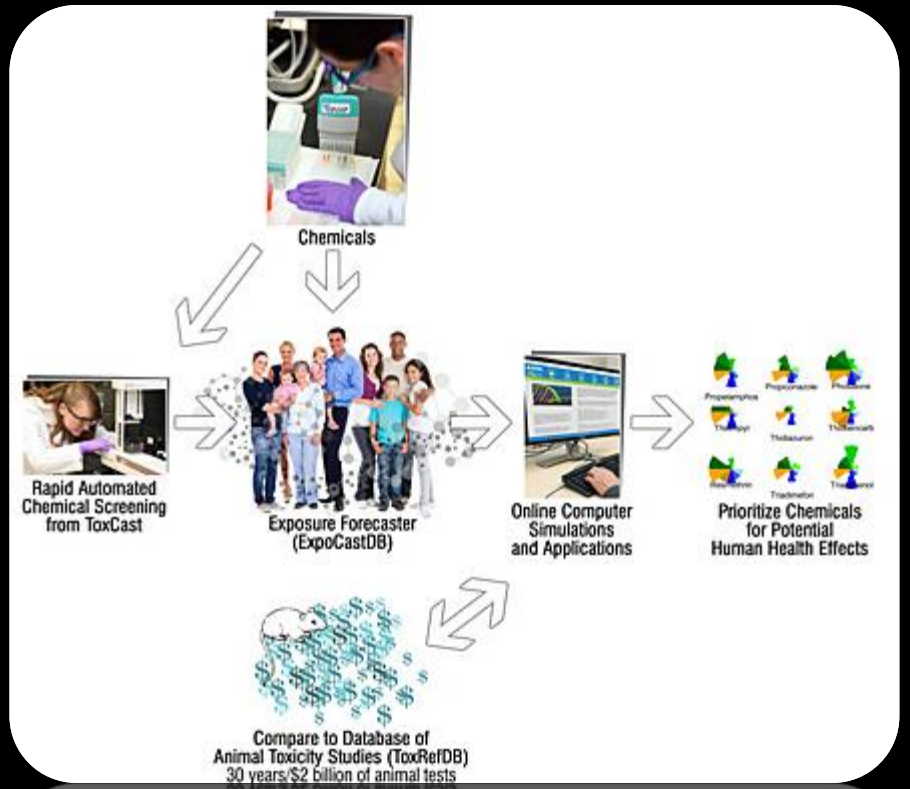
Up Regulated



Down Regulated

USEPA'S TOXCAST PROGRAM

- ToxCast has evaluated over 2,000 chemicals from a broad range of sources including: industrial and consumer products, food additives, and potentially "green" chemicals that could be safer alternatives to existing chemicals.
- Chemicals were evaluated in over 700 high-throughput assays that cover a range of high-level cell responses and approximately 300 signaling pathways.



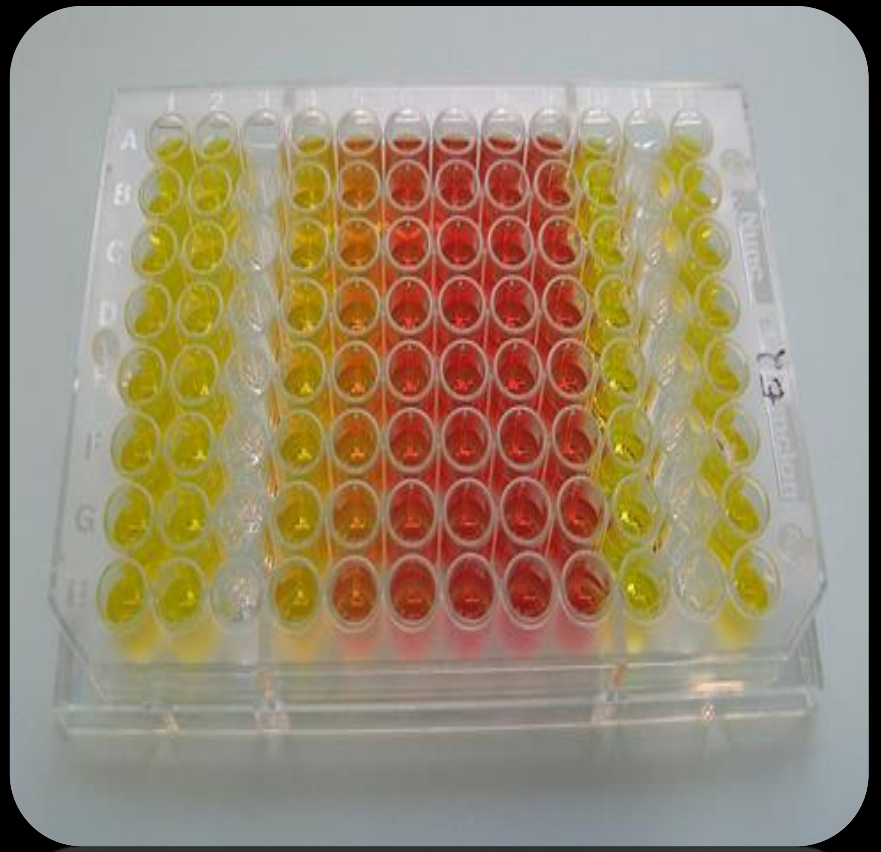
WHAT DID WE FIND OVERALL?

It is likely that these exhaust fumes as well as those from gasoline engines have been captured in this study.

Further, the site is less than 5 km from the Spy Hill landfill.

It is not known what has caused the results of this test to show estrogenic effects; however, it is clear that these results cannot purely be just the result of what has been captured in the discreet analyses.

In other words, part of the picture is missing and there have to be some chemicals that have yet to be accounted for in these samples.



DIESEL FUMES…SO WHAT?

- Diesel engine exhaust fumes have been shown to be particularly harmful to human health.
- Exposure in-utero exposure to fossil fuel combustion has been definitively linked to the development of childhood cancer.
- Prenatal exposure to air pollution has been hypothesized to affect the unborn child through oxidative stress or mechanism involving inflammatory processes.
- Evidence also exists that prenatal exposure to ambient air pollution increases the risk for preterm delivery, fetal growth deficit and cardiac birth deficit , higher respiratory needs at birth and airway inflammation of newborns.

AIR PARTICULATES

- What has been captured in the analytical results is likely the result of adsorbance to fine particulates. Particulate matter (PM2.5) values were measured at 18 µg m^3, less than the 30 µg/m^3 as a 24-hour average concentration guideline within Alberta.

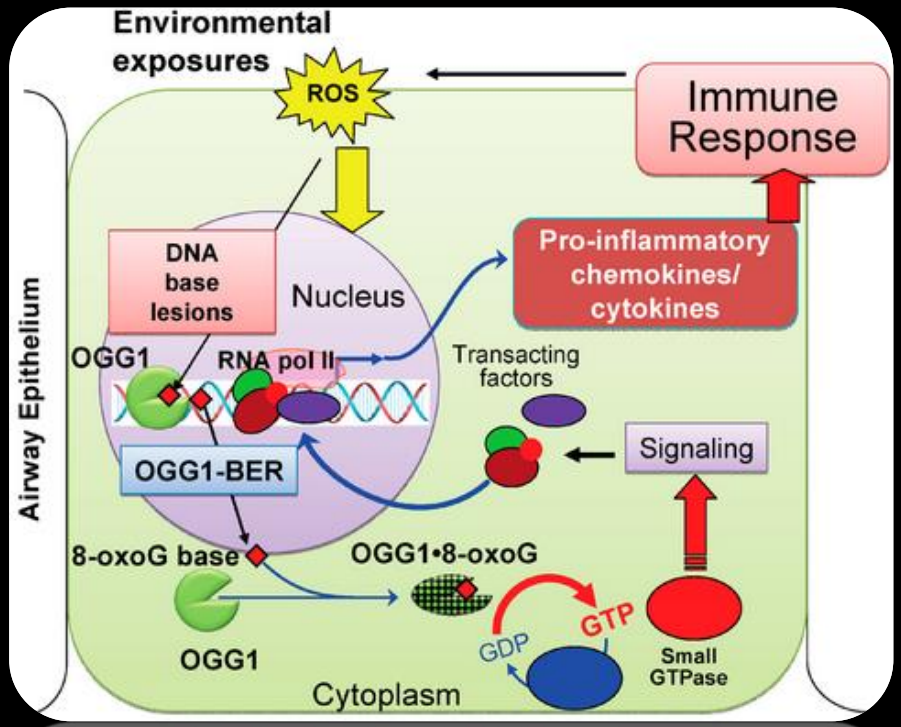
Relevance

- Over 104,000 chemicals have been introduced with few studied for toxicities and only a handful for their interactions.
- The human cost is a reduction of 8.8 years of life for the average person due to the effects of these toxicants which represents 10% of most people's lives.
- **As shown in this study, it is possible for risks to exist even if intensive analytical testing is performed – for what does it all mean? What actually constitutes too much?**

AIR POLLUTION AS A SOURCE OF CHRONIC DISEASE

- Recent reports, however, reveal the presence of dozens of toxic chemicals in Canadian adults and children, including heavy metals, pesticides, dioxins, flame retardants, and other persistent organic pollutants.
- Most chronic diseases have many etiologies, resulting from lifestyle, socioeconomic, environmental, cultural, and genetic determinants interacting over the course of a person's lifetime.

It is a challenge to accurately determine the burden of disease attributable to adverse environmental exposures.



AIR POLLUTION AS A SOURCE OF CHRONIC DISEASE

- The potentially long induction time between environmental exposures and the onset of health effects adds to the difficulty of establishing causation .
- Air pollution can contribute to angina, myocardial infarction, arrhythmias, and congestive heart failure causation.
- The pathophysiology linking particulate exposure to death includes pulmonary inflammation, accelerated atherosclerosis, and cardiac dysfunction causation.

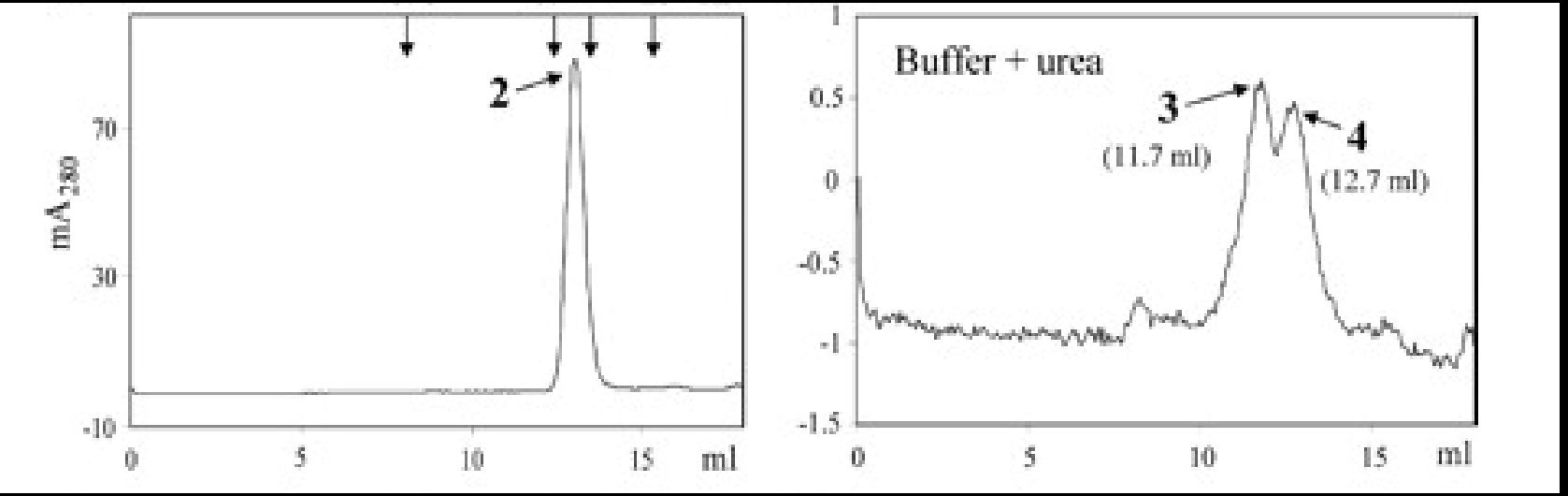
Reality: Conventional practitioners in Canada have no resources and little training to be able to diagnose or recognize environmental determinants of chronic disease.

CHRONIC DISEASE IN CANADA

- Rates of diseases with potential links to chemical exposures have been increasing nationwide.
- Asthma in children under age five has increased by 160%
- Autism has increased by 1000% since the mid-1980s
- Congenital misplacement of the urinary opening in the penis, has increased by 100% and now affects one of 125 male babies born
- Cancer in children has increased by 26%
- Acute lymphocytic leukemia (62%)
- Brain and nervous system cancers (50%)
- Testicular cancer in young men has increased by 85% and is now the most common cancer in men ages 15–35

As per the American Cancer Society, only 5–10% of all cancers can be attributed to inherited factors; the rest occur from environmental exposures and other damage throughout our own lifetimes.

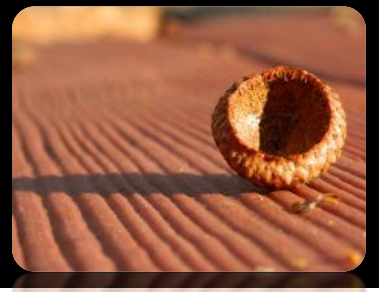
NEXT STEPS: LC/MS QTOF



Quantum Time of Flight LCMS **Conventional Methods**

- A GC-APCI source can be added on to connect the QTOF to a GC so we can do both GCMS and LCMS on one instrument.

IN A NUTSHELL…

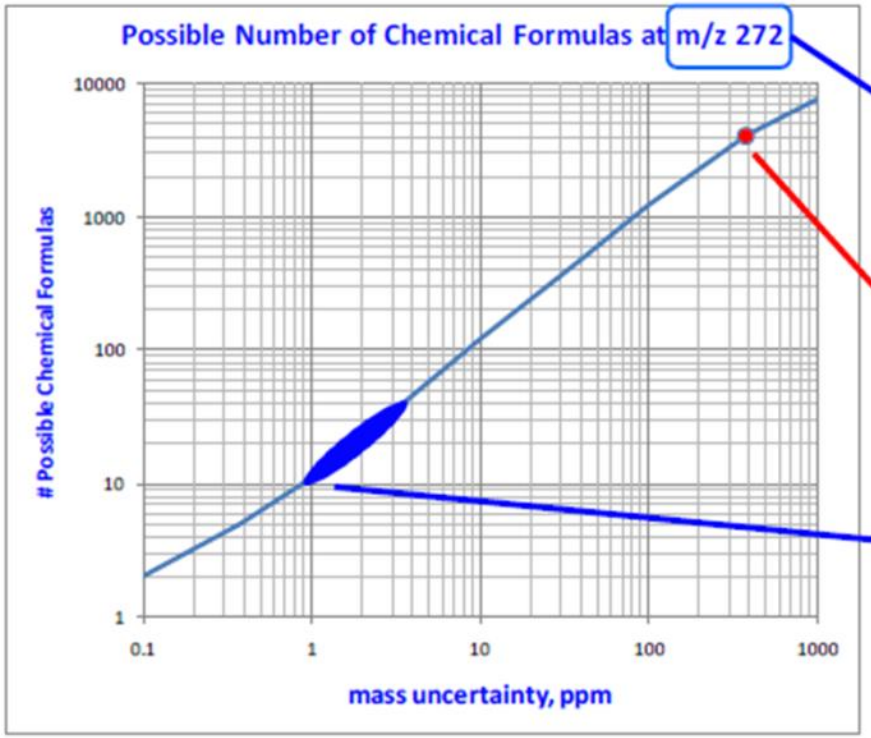


Agilent Technologies

LC/MS INSTRUMENTS

6560 Ion Mobility Q-TOF LC/MS

Accurate Mass Reduces the Number of Possible Chemical Formula



Octafluoronaphthalene (CAS 313-72-4)

$C_{10}F_8$ = 271.98667

mass uncertainty		# of Possible Formulas
ppm	amu	
1000	0.3	7657
368	0.1	4050
100	0.03	1223
37	0.01	466
10	0.003	120
4	0.001	43
1	0.0003	11
0.4	0.0001	5
0.1	0.00003	2

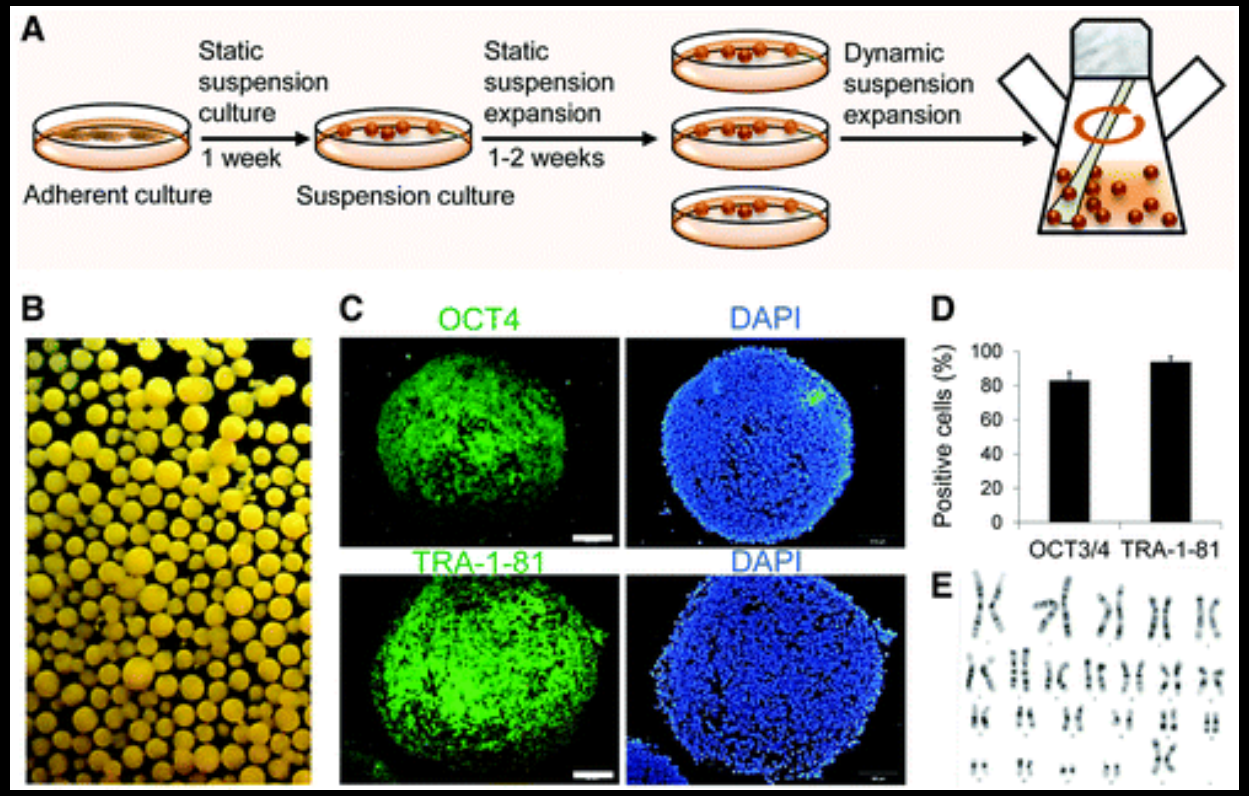
Formulas made of: C,H,N,O,F, & Cl

Accurate mass reduces risk of investing effort on the wrong molecule

WHAT DID WE FIND?

- Glyphosate – not a conventional parameter
- 2,682,656 kg are sold in the province of Alberta, per year.
- This is 3 times more than the next most used herbicide, MCPA, and 3.5 times more than 2,4-D, the third most common pesticide.
- Glyphosate can induce excessive consumption and wasting of glutathione and ascorbate.
- These two antioxidants are at the center of the antioxidant recycling network that protects delicate cell components from free radical oxidative damage during physiologic homeostasis and immune tolerance.
- Once antioxidants are selectively depleted, free radical damage can "run rampant" in oxidizing and making dysfunctional important cell systems

CHEMICALS WIDELY "KNOWN" TO BE SAFE…OR ARE THEY?



(Samsel & Seneff, 2013)

Human cell cultures exposed at low-levels to theoretically "non-toxic" RoundUp (glyphosate) – a chemical that exists on almost all vegetables grown in existence today.
0.5ppm – endocrine disruption.
10 ppm – cytotoxic effects and transcription errors

BIOMONITORING – A GOOD FIRST STEP

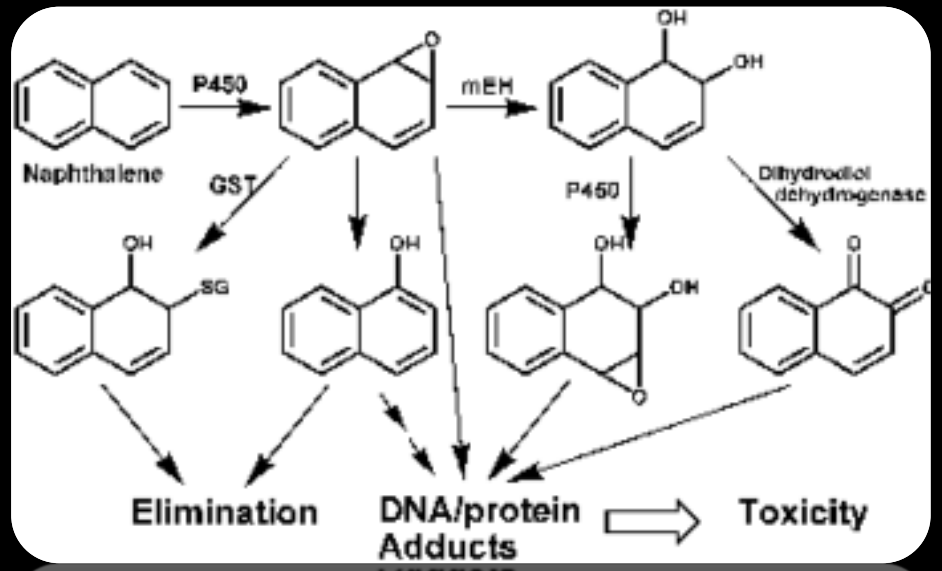
While many chemicals are being monitored by Canada and the United States, the full extent of their potential for harm, especially in sensitive individuals, is still unknown.

There are potentials for synergistic and additive effects, and the differences that are caused by the individual genome. The quantification of these chemicals does not prove causation.

WHY THIS IS IMPORTANT

Even chemicals that are widely thought to be readily metabolized can be compromised with concomitant exposure to other chemicals. For example, lead has been shown to interfere with the toxicokinetics of naphthalene metabolism leading to lipophilic bioaccumulation. Naphthalene is widely believed to be fully metabolized, but clearly is not in the presence of additional toxicants.

- **Simply testing for the levels of toxicants in people is not sufficient.**

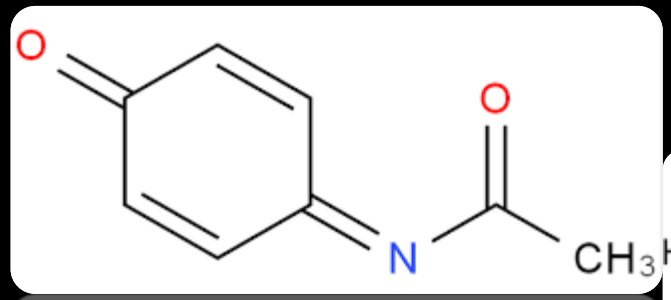


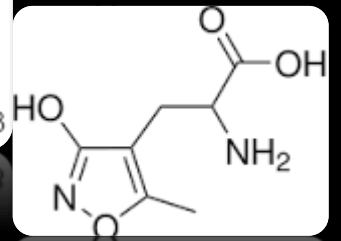
WHO IS AT RISK?

This is potentially the case with children with neurodevelopmental disabilities, who have metabolic detoxification impairments already, and could increase their risk for further injury with heightened bioaccumulation of toxic pollutants.

WHAT SHOULD BE TESTED?

- Certain chemicals that were not tested within any biomonitoring programs should also be included, such as AMPA, the metabolite of glyphosate, and NAPQI, the metabolite of acetaminophen.
- This is important because this represents a realistic and much more affordable set of analysis than what it would cost to run all of these analytes individually.
- Those who are found to be high in these compounds should then further be investigated for liver enzyme precursors other applicable compound classes.





IS IT REALLY THAT BIG A DEAL?

- 1 in 6 children have a neurodevelopmental disability (CDC, 2014)
- 1 in 68 children are born with autism (CDC, 2014)
- The level of children who are considered "gifted" continues to decrease, while the level of children who are considered "cognitively challenged" continues to increase
- Childhood cancers are increasing, particularly leukemia and brain cancers (PHAC, 2014).
- The lifetime risk of diabetes is now 40 percent (Layden et al., 2005).
- The expected life span of the next generation is expected to be between 5 to 20 years less than their parents (New England Journal of Medicine, 2005)

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LITTLE THINGS DO MATTER