Non-Regulated Contaminants: Emerging Issues

Christian G. Daughton, Ph.D.

Chief, Environmental Chemistry Branch

Environmental Sciences Division

National Exposure Research Laboratory

Office of Research and Development

Environmental Protection Agency

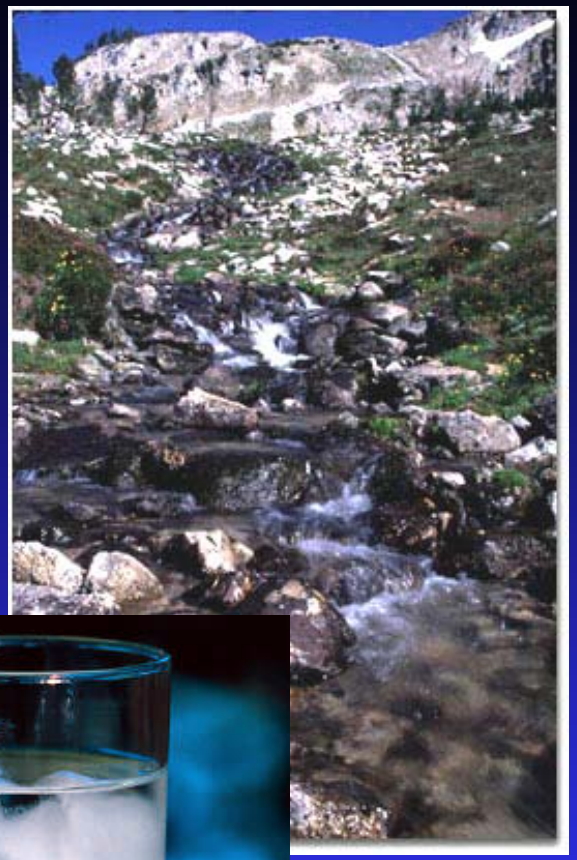
Las Vegas, Nevada 89119

daughton.christian@epa.gov

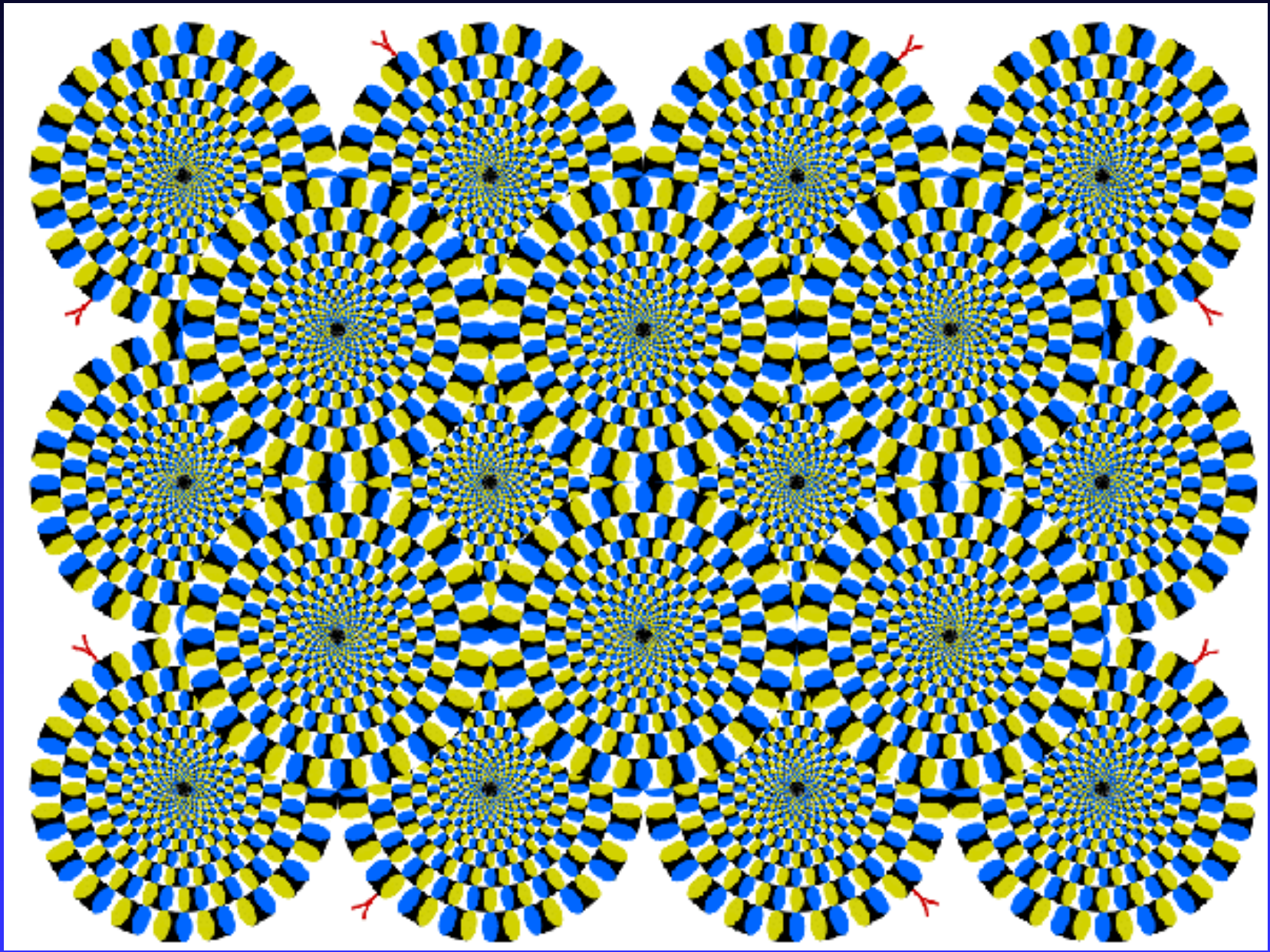
U.S. EPA Notice

The U.S. Environmental Protection Agency (EPA), through its Office of Research and Development (ORD), funded this research and approved the materials that formed the basis for this presentation. While the text for this presentation has been peer reviewed by EPA, the oral narrative has not.

Which water would you choose ?
Recycled Sewage or Snow Melt ?



Perception and *Reality* often do not comport



© Akiyoshi Kitaoka

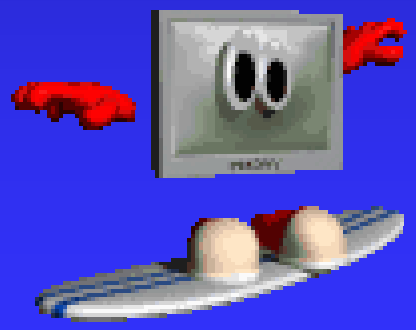
Background materials for this presentation available:

http://www.epa.gov/nerlesd1/chemistry/ppcp/images/iom-2003.pdf

Non-Regulated Contaminants: Emerging Research.

Existing and Future Pollutants in Water Supplies:

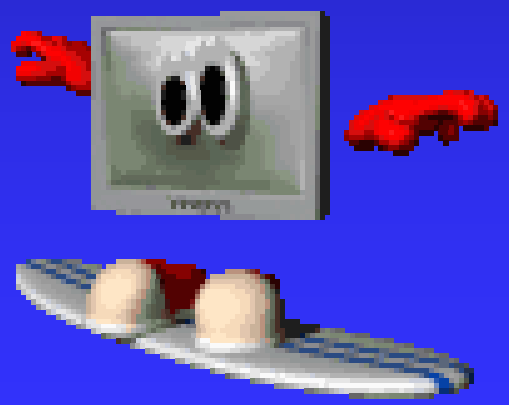
Old Pollutants, New Concerns — New Pollutants, Unknown Issues



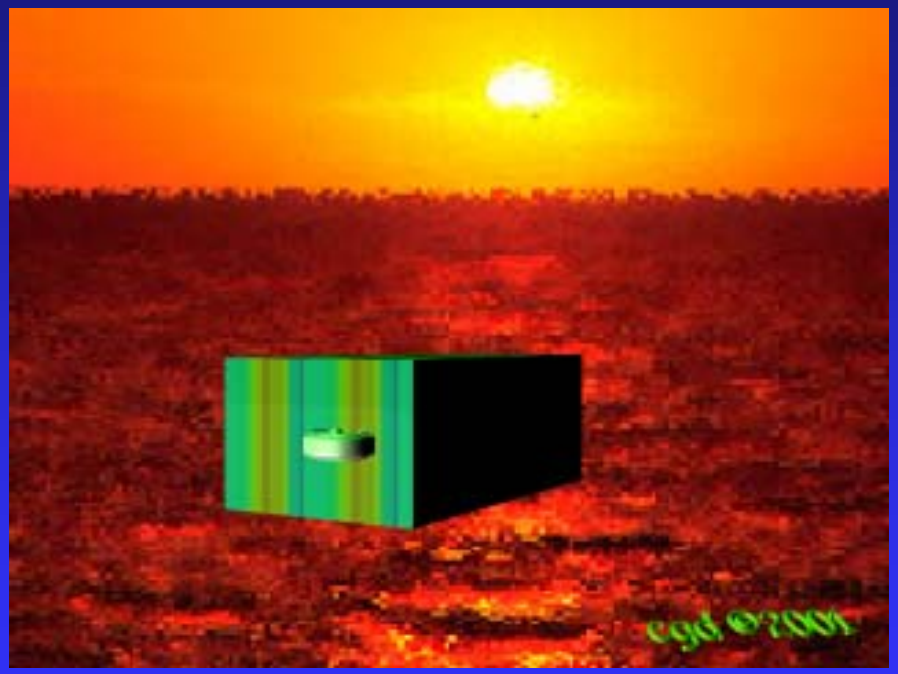
Pharmaceuticals and Personal Care Products - - *PPCPs*

Wealth of resources available at the U.S. EPA's ***PPCPs* web site:**

http://www.epa.gov/nerlesd1/chemistry/pharma



What is meant by "*Emerging*" *Pollutants* ?



"Emerging" *Pollutants* vs. Emerging *Knowledge*

The vast majority of all "emerging" pollutants are not new to the environment:

- **Two major sources for pollutants that are truly "new" to the environment**:
  - Chemicals newly introduced to commerce (e.g., new drugs or pesticides).
  - New anthropogenic processes (e.g., gallium arsenide quantum dots).
- **Previously unrecognized pollutants can come to our attention as a result of**:
  - New advances in chemical analysis (e.g., "non-target" identification).
  - Ability to detect existing pollutants at ever-lower concentrations (e.g., N-nitrosodimethylamine - NDMA).
  - Exploring environmental "compartments" not previously considered (e.g., foods as a significant source of acrylamide).

The Chemical Universe

The *KNOWN* Universe

- As of 28 September 2003, over 22 million organic and inorganic substances had been documented.

(indexed by the American Chemical Society's Chemical Abstracts Service in their CAS Registry; excluding bio-sequences such as proteins and nucleotides)

- Represented a 6% increase over the prior 9-month period.
- Of the 22 million known chemicals, nearly 6 million were commercially available.
- Of these, only about a 0.25 million (227,000) were inventoried or regulated by numerous government bodies worldwide - - representing less than 4% of those that are commercially available or 1% of the known universe of chemicals.

http://www.epa.gov/nerlesd1/chemistry/pharma/critical.htm

The Chemical Universe

The *POTENTIAL* Universe

- While the *KNOWN* universe of chemicals might seem large (22 million), the universe of *POTENTIAL* chemicals (those that could possibly be synthesized and those that already exist but which have not yet been identified) is unimaginably large.

How many distinct organic chemical entities could hypothetically be synthesized and added to a seemingly limitless, ever-expanding chemical universe?

- By limiting synthesis strictly to combinations of 30 atoms of just C, N, O, or S, **more than 10^{60} structures are possible !**

- Expanding the allowable elements to other heteroatoms (e.g., P and halogens), the limits to the numbers of possible structures defies imagination.

“PBTs”, “POPs”, “BCCs”: Only one part of the risk puzzle?

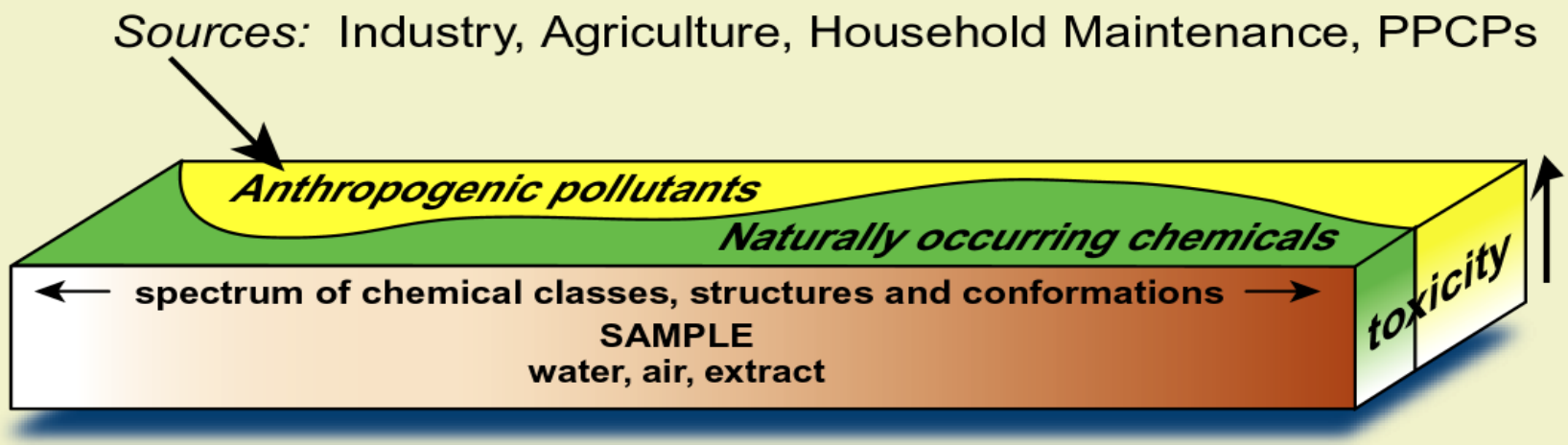
Since the 1970s, the impact of chemical pollution has focused almost exclusively on conventional “priority pollutants,”† especially on those collectively referred to as “persistent, bioaccumulative, toxic” (PBT) pollutants, “persistent organic pollutants” (POPs), or “bioaccumulative chemicals of concern” (BCCs).

The “dirty dozen” is a ubiquitous, notorious subset of these, comprising highly halogenated organics (e.g., DDT, PCBs).

The conventional priority pollutants, however, are only one piece of the larger risk puzzle.

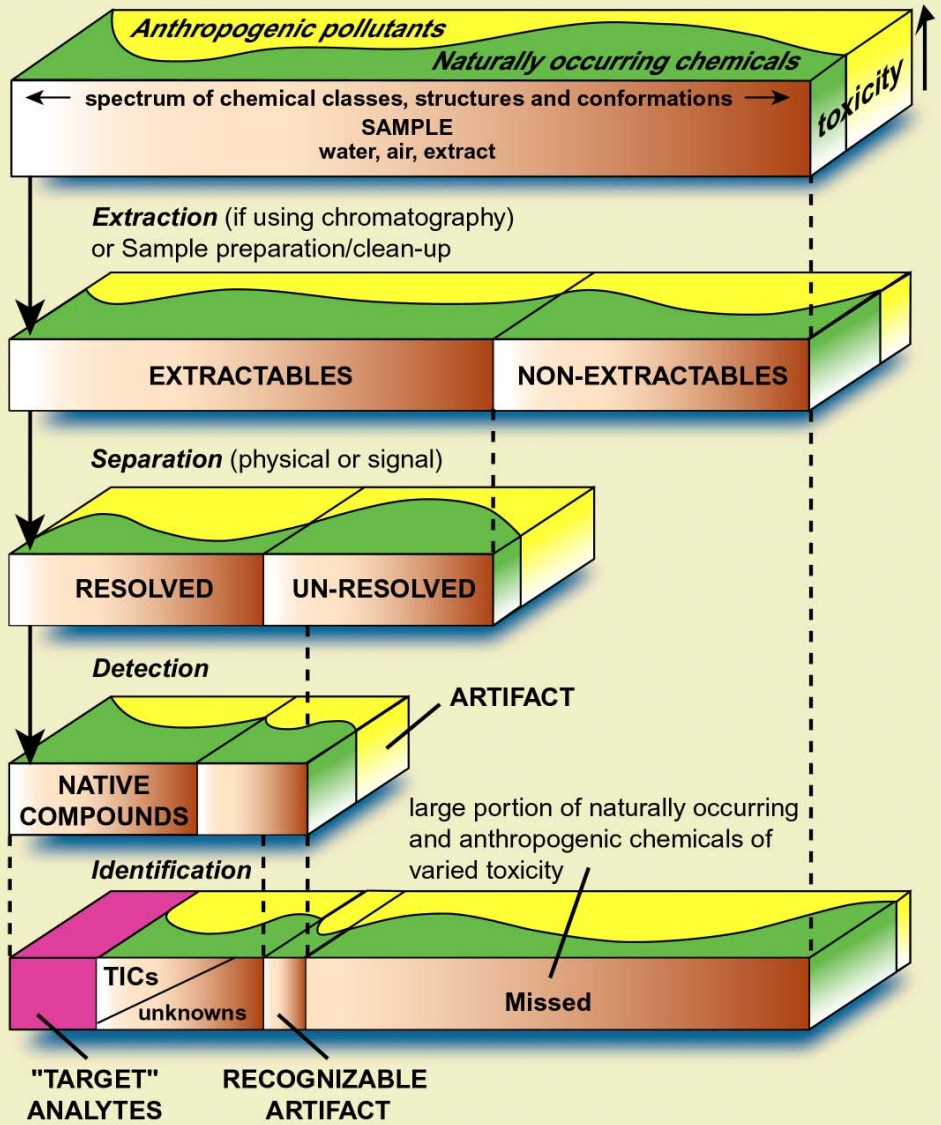
† it is important to recognize that the current “lists” of priority pollutants were primarily established in the 1970's in large part for expediency — that is, they could be measured with off-the-shelf chemical analysis technology. Priority pollutants were NOT necessarily selected solely on the basis of risk.

Universe of Chemicals in the Environment



274odc02-figure 1

Limitations and Complexity of Environmental Chemical Analysis



TICs = tentatively identified compounds

C.G. Daughton
U.S. EPA July 2002

274odc02-figure 2

Chemical Analysis Output for a Typical Environmental Sample

"TARGET" ANALYTES

RECOGNIZABLE ARTIFACT

large portion of naturally occurring and anthropogenic chemicals of varied toxicity

TICs = tentatively identified compounds

C.G. Daughton
U.S. EPA July 2002

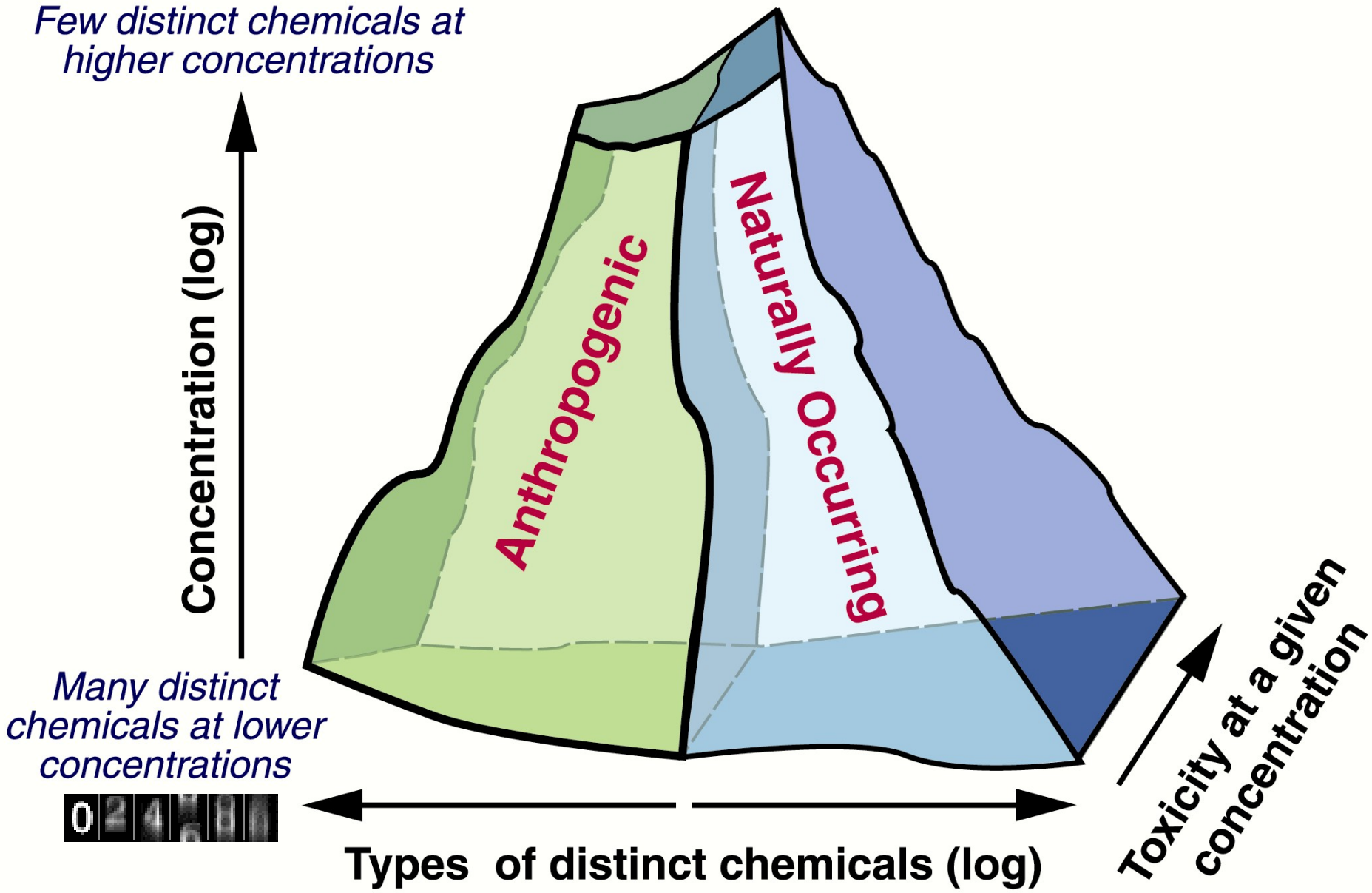
Prevalence of Xenobiotic Occurrence: Some Possible Generalizations Regarding Ubiquity

- The lower the concentration, the higher the probability of larger numbers of distinct chemicals occurring
- **Exponentially more types of chemicals occur at exponentially lower concentrations** (*does the distribution of chemical types versus their concentrations follow a power law, as shown for such a wide array of other phenomenon?* e.g., see: M. Buchanan "Ubiquity", Crown Publishers 2000)
- At the very lowest concentrations (zeptomolar to yoctomolar, zM - yM), the off-the-cuff truism may apply:

"***Everything can be found everywhere***"

continued -

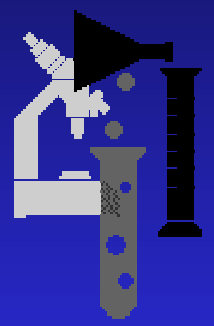
Prevalence/Distribution of Xenobiotic Occurrence



Can risk be assessed in a truly holistic manner without knowing the actual exposure universe?

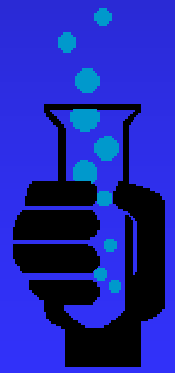
Einstein on:
Environmental Monitoring

"Not everything that can be counted counts, and not everything that counts can be counted." (oft attributed to Albert Einstein)



corollary for environmental monitoring

Not everything that can be measured is worth measuring, and not everything worth measuring is measurable.



further truisms regarding *Environmental Monitoring*

- What one finds usually depends on what one aims to search for.
- Only those compounds targeted for monitoring have the potential for being identified and quantified.
- Those compounds not targeted will elude detection.
- The spectrum of pollutants identified in a sample represent but a portion of those present and they are of unknown overall risk significance.

What portion of overall risk is contributed by unregulated water pollutants?

Unregulated Pollutants and the "*4Ts*"

- An organism's exposure "envelope" can encompass numerous pollutants at any point in time.
- But to what degree do we need to know the identities and concentrations of all the xenobiotics to which an organism is exposed?
- Theoretically, there are multiple dimensions to consider in assessing holistic risk posed by exposure.
- Knowing the identities and doses of the chemical stressors (including both *regulated* and *unregulated* pollutants) that compose the immediate exposure envelope accounts for but two dimensions - - the "Toxicants" and their "Totality".

continued >

Unregulated Pollutants and the "*4Ts*"

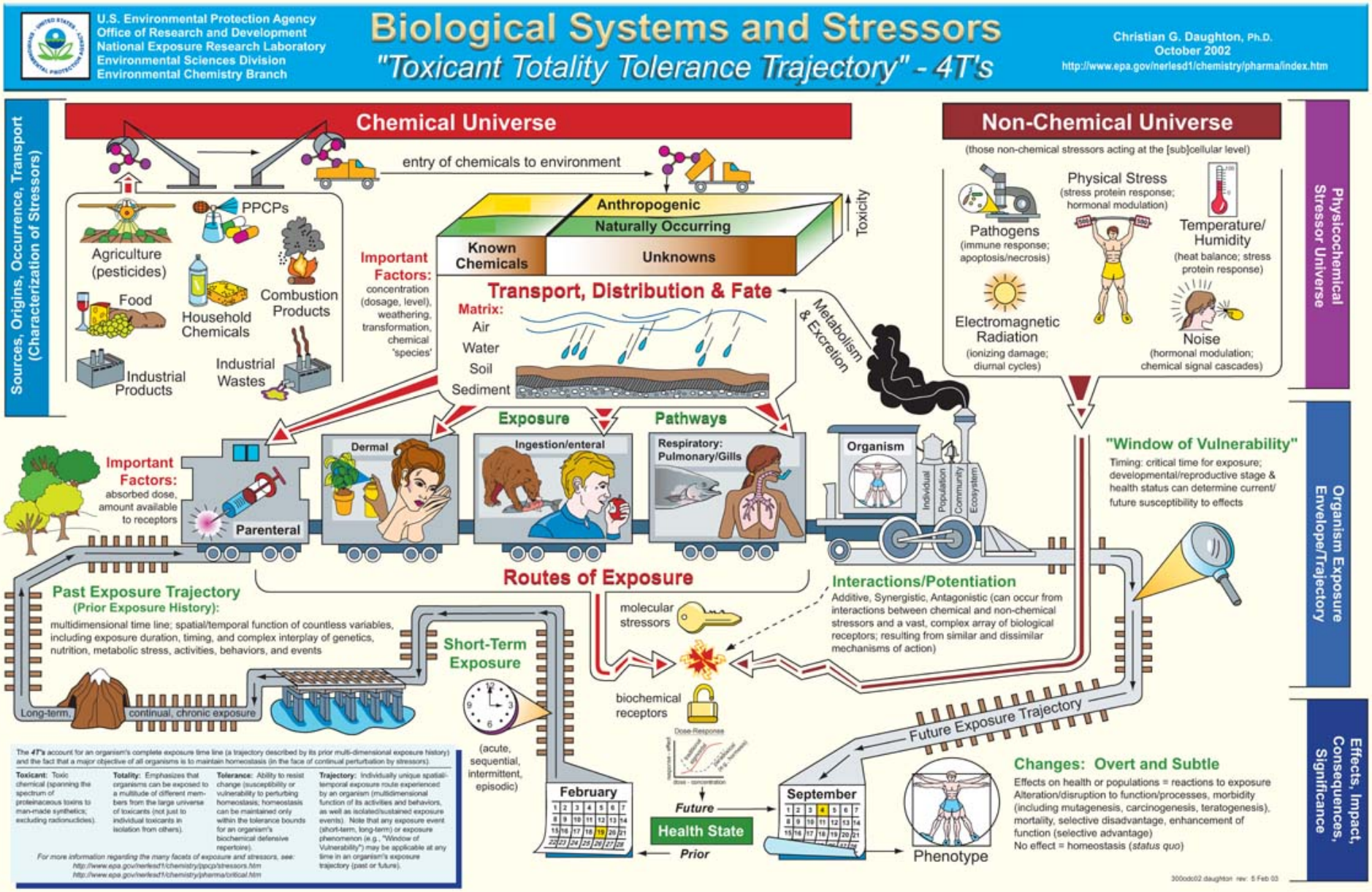
There are two other dimensions - - "Tolerance" (resistance of homeostasis to perturbations) and "Trajectory" (dynamic variations in stressor types and concentrations over time).

The "4Ts" ("Toxicant Totality Tolerance Trajectory") form the foundation for understanding the hypothetical, overall "true" risk - - the risk reflected by the sum total of exposure to all toxicants (anthropogenic and naturally occurring) throughout a multi-dimensional space and time exposure "trajectory."

http://www.epa.gov/nerlesd1/chemistry/ppcp/stressors.htm

continued >

Unregulated Pollutants and the "*4Ts*"



- concluded -

Toxicity of Complex Environmental Mixtures:

Poses Major Unanswered Questions

Questions regarding *Toxicant Totality*

Is the overall toxicity (or the spectrum of unique toxic effects) of a complex mixture caused by few or many chemical constituents?

And do these constituents comprise a small or large fraction of the total dissolved mass?

Exposure to Multiple, Trace-Level Xenobiotics below Known Effects Levels

Potential Toxicological Significance as a Result of:

(1) Potential for **additive effects** from multiple agents sharing common mechanisms action (MOAs). Individual concentrations combine to exceed an effects level.

(2) Possible **interactive effects**, especially synergism, where combined action exceeds the sum of individual effects.

(3) **Hormesis** – Effects below NOELs. Paradoxical "U-shaped" dose-response curves.

continued >

Potential Toxicological Significance as a Result of:

(4) Comparatively little research performed at **extremely low concentrations** (nM-pM and below). Some agents have ability to impart previously unrecognized effects at "ultra-trace" concentrations.

(5) **Non-target species receptor repertoires** not well characterized. Variation in receptor repertoires across species, and unknown overlap with humans leads to countless questions regarding potential effects.

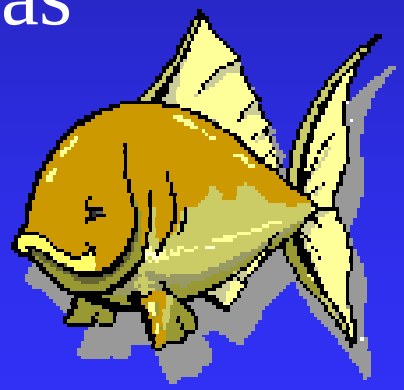
(6) Susceptible **genetic outliers** within species.

(7) **MOAs not fully understood**. Even most drugs can each have a multitude of effects. Most MOAs remain to be discovered.

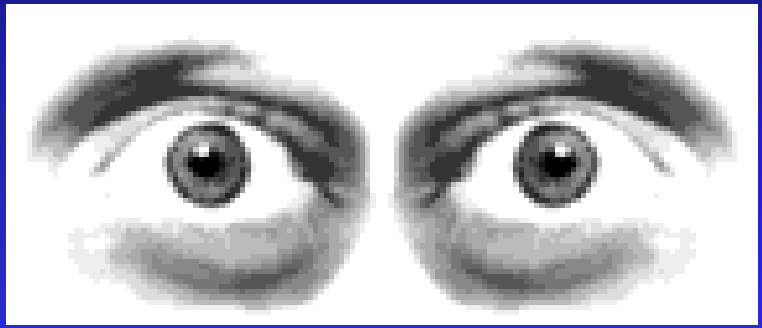
- concluded -

Re-evaluation of "Persistence"

Chemicals continually infused to the aquatic environment via sewage outfalls essentially become "persistent" pollutants even if their half-lives are short — their supply is continually replenished. These can be referred to as ***pseudo-persistent* chemicals (P2's)**.



Peeking at the Future



Critical Importance of *Futuring & Anticipatory Research*

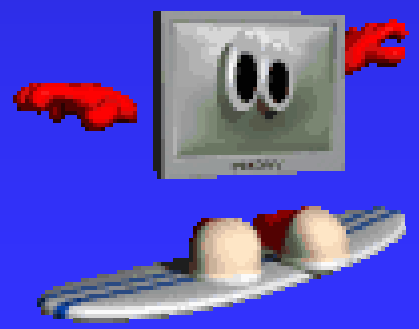
Important to design and implement a range of mechanisms for providing insight as to those types of pollutants and sources that could emerge in the future.

Pollution Prevention and Stewardship programs can be less costly than remediation (Precautionary Principle).

continued >

Wealth of materials and links for:
Environmental Stewardship of PPCPs
at the U.S. EPA's web page on the
Green Pharmacy:

http://www.epa.gov/nerlesd1/chemistry/ppcp/greenpharmacy.htm



Questions Regarding Decaying and Inadequate Water Infrastructure

2003 Report Card for America's Infrastructure

American Society of Civil Engineers (ASCE)

(http://www.asce.org/reportcard/index.cfm?reaction=full)

Nationwide grades of "D" assigned for both drinking water and wastewater infrastructures

(http://www.asce.org/reportcard/index.cfm?reaction=full&page=2)

Over $20 billion dollars annually is the estimated need for rectifying the nation's degenerating water/waste infrastructures:

"The nation's 54,000 drinking water systems face an annual shortfall of $11 billion needed to replace facilities that are nearing the end of their useful life and to comply with federal water regulations. Non-point source pollution remains the most significant threat to water quality."

"The nation's 16,000 wastewater systems face enormous needs. Some sewer systems are 100 years old. Currently, there is a $12 billion annual shortfall in funding for infrastructure needs in this category; however, federal funding has remained flat for a decade. More than one-third of U.S. surface waters do not meet water quality standards."

Key to Maintaining & Improving the Public's Confidence in Water Supplies

Growing pressures to re-use wastewaters for drinking

"Increasingly Smaller Recycle Loops": Ever-shortening spatial & temporal hydraulic connectivity between point of wastewater discharge and point of use for drinking will pose serious challenges for ensuring human safety and for framing how risk is perceived by the consumer.

Two Major Issues:

Groundwater Recharge (both indirect and direct)

De-Centralized Water Re-Use - - "Toilet-to-tap"

Water Re-Use

Communicating Risk More Effectively

Growing importance of public acceptance of wastewater re-use for human consumption (especially "toilet-to-tap" re-use programs) highlights the need for vastly improved approaches to risk communication.

- Highlights need for scientists to better convey the significance of their work to the public.
- Points to need for exploring more effective means for aligning the long-troubling disconnect of disparate views of risks as held by scientists versus the public: *real hazard vs. risk perception*.
- Receiving little attention is the more substantive role that could be played by the cognitive sciences (social scientists and psychologists) in helping to bridge the communications gap.

Early-Warning Water Monitoring

- Unregulated (including "emerging") pollutants could provide critical missing pieces for the larger holistic risk puzzle.
- Designing and implementing *early-warning water-monitoring systems* could prove essential for providing a better understanding of the *4Ts*.
- Low-cost, rapid monitoring is theoretically possible for non-target pollutants with the use of analytical approaches based on "*change detection*" - - using changes in pollution "fingerprints" to *focus solely on those unknown contaminants that are newly present*.

continued >

Early-Warning Water Monitoring

Early-warning, change-based water monitoring could also prove essential for assisting with five other critical issues facing society.

(1) *Homeland Security* - - Minimizing chances of widespread exposure resulting from sabotage of water systems.

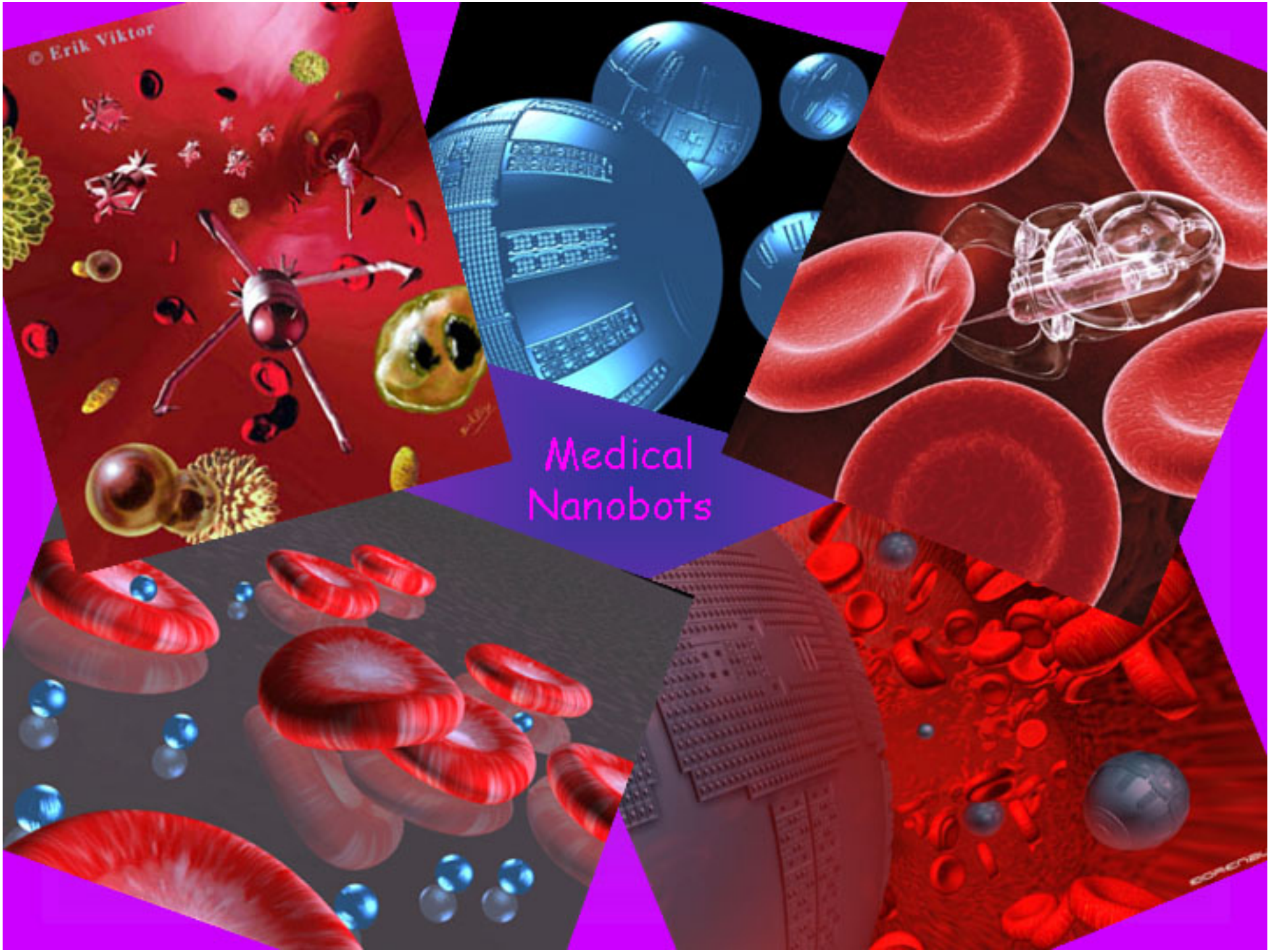
(2) *Water Re-use/Recycling* - - Solidifying & maintaining public trust in water supplies (critical for attaining public acceptance of water reuse).

(3) *Detecting unanticipated impacts of technology on the environment* - - impacts have traditionally gone undetected until a pollutant establishes a widespread presence in the environment.

(4) *Enhanced science literacy* (changing consumer behavior & perceiving of risk) - - improved public understanding that chemicals derived from consumer actions and activities can gain immediate access to the environment

(5) *Advanced warning of new trends in drugs of abuse* - - Previously unknown trends in usage of drugs of abuse (increases and reductions) can theoretically be revealed by monitoring sewage.

- concluded -


© Erik Viktor
Medical
Nanobots

SUDUX: *Structurally Undefinable Ubiquitous Xenobiotics*

Importance of Developing the Means to Evaluate and Monitor "Undefinable" Pollutants

- The widespread emergence in consumer products of new nanomaterials poses a host of currently unanswerable questions regarding their environmental chemistry and environmental toxicology.
- In particular, the natural weathering or environmental transformation of these materials holds the potential to yield numerous additional, structurally undefinable products.
- These substances could pose numerous challenges to their monitoring in the environment.

Avoiding Future Pollution: Contaminant "Musical Chairs"

Need to minimize practices designed simply for the storage or diversion of pollutants:

- "**Pollution Postponement**" (e.g., landfills)
- "**Pollution Redirection**"

(e.g., concentrated reject brine from water treated by membrane filtration; biosolids applied to land)

Questions

feel free to contact:

Christian Daughton, Ph.D.

Chief, Environmental Chemistry Branch

Environmental Sciences Division

National Exposure Research Laboratory

U.S. Environmental Protection Agency

daughton.christian@epa.gov

702-798-2207

http://www.epa.gov/nerlesd1/chemistry/pharma/

prepared for:

From Source Water to Drinking Water: Emerging Challenges for Public Health

National Academies, Institute of Medicine, Roundtable on Environmental Health Sciences, Research, and Medicine (EHSRT), Workshop #5, 16 October 2003, Washington, DC

Christian Daughton, Ph.D.

Chief, Environmental Chemistry Branch

Environmental Sciences Division

National Exposure Research Laboratory

U.S. Environmental Protection Agency

daughton.christian@epa.gov

702-798-2207

prepared 7 October 2003