Emerging Contaminants – State of the Science in The U.S.A.

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Japan - U.S. Joint Conference
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Our concern about the unintended consequences of chemicals has deep roots and those roots lie in our relationship to technology. For many years pundits have predicted that the human population would exhaust the earth's resources and that, civilization as we know it, would perish. First Thomas Malthus in 1798 and more recently Paul Erlich in 1969. We've overcome these predictions through the application of technology. But many worry about the unintended consequences of that same technology. The more powerful that technology, the greater are the consequences implied. Chemisty has been at the heart of our technological advance, so it is not surprising that a great deal of energy has been directed toward the unintended consequences of those chemicals. Our chemical revolution began in earnest between 1920 and 1950. Some approximate dates: TNT ~ 1900, Bakelite ~ 1922, Penicillin ~1928, PCBs ~ 1929, Polystyrene ~ 1931, Alkylbenzene sulfonate (detergent) ~ 1933, Nylon ~1935, DDT ~ 1939, Toxaphene ~ 1942, Tetracycline & Chlordane ~ 1948, Erythromycin 1949, and Polyurethane ~ 1952. Truly these chemicals and the many that followed have had a profound effect on our standard of living.

But just as these chemicals worked miracles in our everyday lives, concerns about their possible unintended consequences, to our public health, and to the environment began to evolve. In the late 1950s, the USPHS did extensive work trying to find a way to assess the level of hydrocarbon pesticides in drinking water sources. Gordon Robeck, Keith Carswell and Jim Symons developed a gravimetric method, the carbon chloroform extract (CCE), and surveyed the nation's water supplies. This lead to the inclusion of recommended limit of 0.2 mg/L for the CCE in the USPHS 1962 drinking water standards.

1962 was also a big year where chemicals in the environment are concerned. It was in that year that Rachel Carson published her book *Silent Spring,* a book that is often cited as the beginning of the environmental movement. Carson wrote about the dangers of pesticides like dieldrin, toxaphene, heptachlor and DDT. Because it challenged many prevailing assumptions, her book was controversial. President Kennedy asked his Science Advisory Committee to review the issues it raised. Ms. Carson came out of that review with a stronger reputation than she had before it began. Carson was a skeptic about technology who said, "Sometimes technological progress is so fundamentally at odds with natural processes that it must be curtailed." Many mark the publication of Carson's book as the moment at which a fundamental struggle began between two segments of society: those seeking a higher standard of living through technical innovation and those concerned about the unintended consequences of these same new technologies. In that sense, the issue of emerging contaminants is 47 years old.

The following are some notable events on that journey. National organics reconnaissance survey (NORS) and the National Organics Monitoring Survey (NOMS) where Robeck and Symons extended their efforts to survey the presence of organics in U.S. drinking waters, taking advantage of new analytical technology. The 1974 Safe Drinking Water Act, largely passed to address concerns about man-made organics in drinking water. In 1974 the discovery, both in the U.S. and in Holland, of the trihalomethanes, synthetic organic compounds resulting from the action of chlorine in drinking water. Subsequent regulatory and monitoring activities on disinfection byproducts continue to this day. The 1976 NRDC Consent Decree and the subsequent 1977 Clean Water Act Amendments identifying the 129 Priority Pollutants. The 1977 discovery of DBCP as a groundwater pollutant and, in 1980 the creation of CERCLA and the idea that all chemicals should be managed from cradle to grave. During that same period, the discovery of solvents like TCE and PCE in groundwater throughout the U.S. In 1986 the regulation of VOCs, the SDWA amendments, SARA, and California's Proposition 65. The Superfund. The discovery of MtBE contamination, spreading much more rapidly than originally envisioned. The unveiling of perchlorate in groundwaters throughout the country. Our latest interest in endocrine disrupters, pharmaceuticals, personal care products, and household chemicals, which began around the turn of our new century, seems only a logical extension of this continuing story.

A quick list of today's constituents of concern shows Herbicides like atrazine and metolachlor, personal care product like DEET and triclosan, household chemicals like caffeine and detergents, industrial chemicals like EDTA and Bisphenol A, Pharmaceuticals like metabolic regulators and antiobiotics, microbes like norovirus and adenovirus and nanoparticles.

Looking just at the organic chemicals among these the author was able to identify in the literature 100 compounds often found in U.S effluents and surface waters:

> 1,4-dichlorobenzene, 1,7-dimethylxanthine, 17 -ethinylestradiol, 17 -estradiol, 2,6-di-t-butyl 1.4-benzoquinone, 2,6-di-t-butyl phenol, 3-t-butyl-4-hydroxy anisole, 4-methyl phenol, 5-methyl-1H-benzotriazole, Acetominophen, Amoxicillin, Androstenedione, Atenolol, Atrazine, Azithromycin, Benzo(a)pyrene, Bezafibrate, Bisphenol-A, Brominated Diphenyl Ether (BDPE), Butylated hydroxyanisole (BHA), Butylated hydroxytoluene (BHT), Caffiene, Carbamazepine, Chloropyrifos, Chlorotetracycline, cholesterol, Ciprofloxacin, Clarithromycin, Clofobric acid, Coprostanol, Cotinine, DDT, Dehydronifedipine, diatrozate, Diazenon, Diazepam, Di-N-butylphthalate, Diclofenac, Dilantin, Diphenhydrmine, Enroflaxicin, erythromycin, Estriol, Estrone, Ethanol, 2-butoxy-phosphate, Ethinyl Estradiol, Ethylenediamine tetra acetic aid (EDTA), Fluoranthene, Fluoxetine, Galaxolide, Gemfibrozil, Hydrocone, Ibuprofen, Indometacine, Iopromide, Ketrprofen, Lincomycin, Lipitor, Meprobamate, Metolachlor,Methadone, Metroprolol, Monesin, Morphine, Musk Ketone,

> Naphthalene, Naproxen, N-N-diethyltoluamide (DEET), Nitrilotriacetate (NTA), Nonylphenol, Nonylphenol poly ethoxylate, Norfloxacin, NDMA, Octylphenol, Octylphenol Poly ethoxylate, Ofloxacin, Oxybenzene,
> Pentoxifyline, Phenytoin, Phthalic anhydride, Phenacetine, Polybrominated diphenyl ethers (PBDE), Predisone, Primadone, Progesterone, Propranolol, Pyrene, Roxithromycin, Salicycllic acid, Sulfadimethoxine, Sulfamethazine, Sulfathomethoxazole, Sulfathiozole, TCEP, TCPP, Testosterone, Tonalide, Triclosan, Trimethoprim & Virginiamycin.

Of these 100 about 1/3rd are compounds we either see or expect we will see with some regularity in drinking water:

> Acetominophen, Atenolol, Atrazine, Azithromycin, Bisphenol-A, Caffiene, Carbamazepine, Ciprofloxacin, Erythromycin, Estrone Ethylenediamine tetra acetic aid (EDTA), Galaxolide, Gemfibrozil, Ibuprofen, Iopromide, Meprobamate, Naproxen, N-N-diethyltoluamide (DEET), nonylphenol, nonylphenol polyethoxylate, Phenytoin, Octylphenol, Octylphenol polyethoxylate, Primidone, Sulfamethoxazole, TCEP, Triclosan, & Trimethoprim

Thirteen of that 1/3rd are particularly persistent, and therefore, candidates for groundwater contamination:

> Bisphenol-A, Carbamazepine, Ciprofloxacin, Ethylenediamine tetra acetic aid (EDTA), Gemfibrozil, Iopromide, Meprobamate, N-N-diethyltoluamide (DEET), nonylphenol, nonylphenol polyethoxylate, Phenytoin, Octylphenol, Octylphenol polyethoxylate, Primidone, & Sulfamethoxazole.

Eleven of that 1/3rd were those most frequently found in recent surveys of U.S. tap waters by SNWA's research lab working for WRF:

> Atenolol, Atrazine, Carbamazepine, Estrone, Gemfibrozil, Meprobamate, Naproxen, Phenytoin, Sulfamethoxazole, TCEP, & Trimethoprim

So how do we manage this? The Current U.S. Model for Environmental Risk Management is derived from work done by the National Academies in the mid-1980s. It specifies a five step process: 1) Hazard Identification, 2) Dose response assessment, 3) Exposure assessment, 4) Risk characterization and 5) Risk management. For years now all environmental scientists and environmental engineers in the U.S. have been trained in this methodology and a substantial inventory of professionals has been developed that specialize in the generation of required dose response and occurrence data and in the application of Risk Assessment procedures following this model. But problems are developing in applying this procedure: problems with its cost and timeliness in particular.

The scientific data required are often not available and when data are available the quality is not what we are accustomed to in the hard sciences. We chose not to directly measure

health-effects in humans, so we test outcomes in other animals. We cannot observe effects at low doses, so we give the animals high doses.
And we use cross-species safety factors and multi-stage models to understand what the results mean. Both are logical, neither can be verified by testing. We suspect that impacts resulting from exposure to one chemical may be affected by exposure to another but we don't understand these complexities well enough to include them in our risk assessments. Most of the analytical methods we use to assess occurrence are target-specific; i.e. we only find what we look for. Hence, we don't know what we don't know. The analytical methods we do have are becoming increasingly sensitive. Increasingly we know something is present without knowing if its presence, at that level, is significant.

It is not surprising that disagreements exist among members of the scientific community about how the data we do have should be interpreted. Nor is it surprising that people don't agree about the significance of the risks identified.
The problem is even more complex when we expand our horizon to consider impacts on the entire eco-system.

Meanwhile, Change is coming at an increasingly rapid pace: driven by population growth, driven by economic growth. Potential new problems are out-stripping the resources we have to address them. This can be illustrated by examining a plot of the growth of the earth's human population. During this author's lifetime, the earth's population has grown from 2.2 to 6.7 billion persons. A review of well-known environmental impacts shows they are of increasing scale: The 1850s waterborne disease affecting thousands, early in the 20th century oxygen depletion affecting the ecology in major rivers, 1950 smog affecting millions in the Los Angeles Basin, the 1970s acid rain across regions of continents, the 1980s the hole in the ozone layer affecting entire hemispheres and now global warming.

We need a risk management scheme that can keep pace with these events. It is time we (the U.S.) re-examined our approach. A dialogue about the proper design of preventative action may be the right place to start. Possible guidelines for precaution:

- Substance is known to be toxic
- Evidence of adverse effects is accumulating
- Substance is not removed by secondary treatment
- Substance is persistent in the environment
- Substance accumulates in the food chain

How might this work with our problem of emerging contaminants? Perhaps the following might be the elements of a appropriate response:

1. Essential tenant: On-going investment is required (no illusion that the "problem" will soon be "solved").
2. Monitor Monitor, Monitor: Develop & maintain lists of compounds; Develop & maintain standard methods of analysis; Conduct regular national surveys; On-going requirements for monitoring by water and wastewater utilities and industry (effluents, influents, groundwater, biota).

3. Cradle to grave management: National program on habits of disposal; On-going research on removal in water and wastewater treatment; Upgrade treatment (both water & wastewater).
4. Find the Bad Actors and Fix them: Identify compounds that persist in the environment, accumulate in the biota, are resistant to treatment, show evidence of toxicity, etc.; Study their toxicity; Find replacements for problem compounds

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Outline

- Historical Perspective
- Constituents Currently Emerging
- Future Perspective
- What Should be Done to Manage Our Risk

Our concern about the unintended consequences of chemicals has deep roots

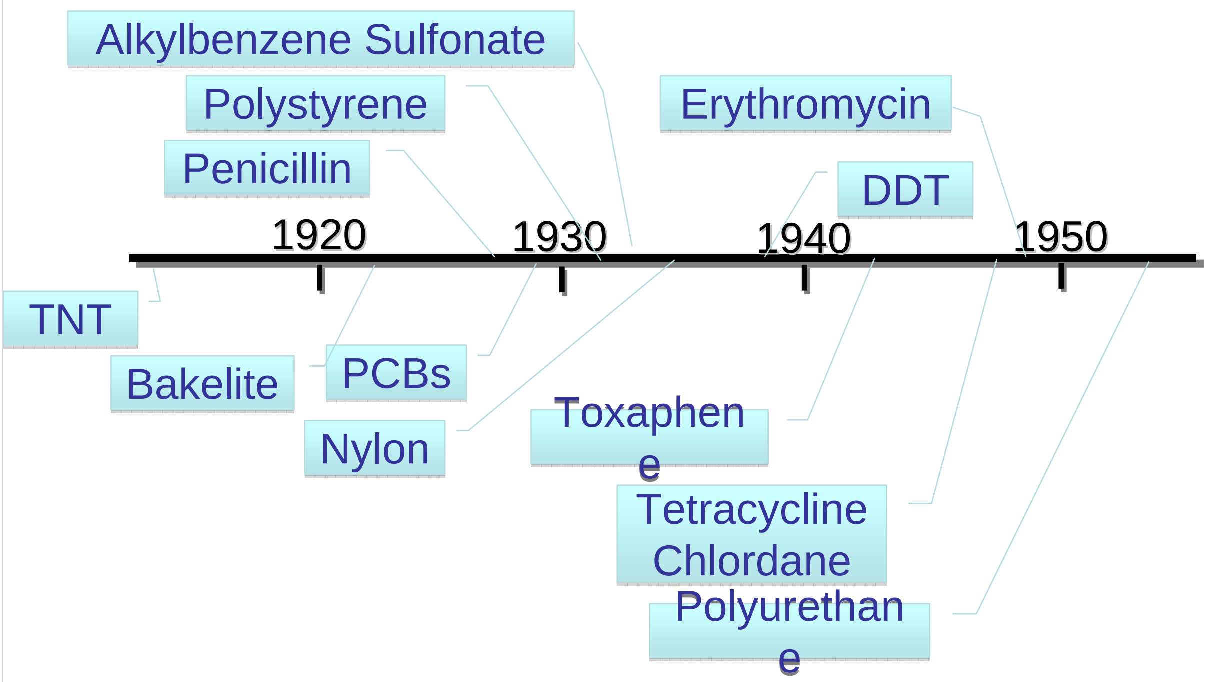
- In 1798 Thomas Malthus predicted we were running out of food (The world population at the time was ~ 950 million)
- In 1969, Paul Erlich predicted we were running out of resources, including food, and that, by 1985 the world population would be reduced to a sustainable level of 1.5 billion people (The world population was then 3.6 billion. Today it is 6.7 billion)

We have overcome these predictions through the application of technology

- Yet many worry about the unintended consequences of that technology
- The more powerful the technology, the greater are the unintended consequences implied
- Chemistry has been at the heart of our technological advance
- So it is probably appropriate that the focus has been on the unintended consequences of those chemicals

Our chemical revolution began, in earnest, between 1920 and 1950

Modern living through chemistry



Truly, these chemicals have changed our standard of living

Concerns about unintended consequences, to public health, and to the environment, began in the 1950s

Early work

- In the late 1950s, the USPHS did extensive work trying to find a way to assess the level of hydrocarbon pesticides in drinking water sources
- They developed a gravimetric method: the Carbon chloroform extract (CCE)
- Gordon Robeck, Keith Carswell & Jim Symons

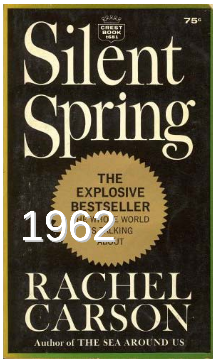
1962 was a big year

1962 was a big year

The USPHS issued 1962 drinking water standards which recommended
the carbon chloroform extract (CCE) at $\leq$ 0.2 mg/L

1962 was a big year

1970 1980 1990 2000



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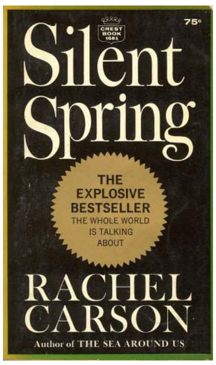

Ms. Carson wrote about the dangers of pesticides like dieldrin, toxaphene, heptachlor and DDT

1962 was a big year

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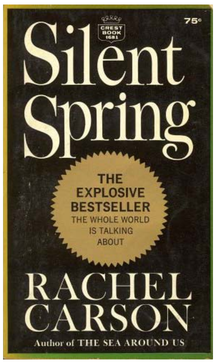


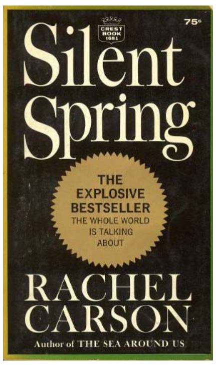
The book was very controversial

President Kennedy had a Science Advisory Committee review the issue

The Committee supported Carson

1962 was a big year

1970 1980 1990 2000



"Sometimes, technological progress is so fundamentally at odds with natural processes that it must be curtailed" - *R. Carson*

1962 was a big year

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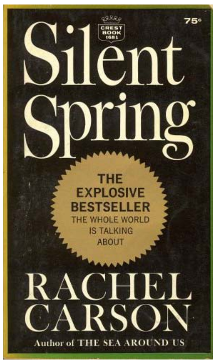


And so began the struggle between:

- people concerned about the unintended consequences of new technologies … and
- people seeking a higher standard of living through technical innovation

That struggle now begins its 47th year

So emerging constitutents is not a new issue

Emerging constituents is not a new issue

- 47 year history:

1970 1980 1990 2000

1974

National Organics Reconnaissance Survey (NORS) - continuing to look for organics in drinking water - but with GC/MS

Emerging constituents is not a new issue

- 47 year history:

1970 1980 1990 2000

1974

NORS

SDWA - protect our drinking water from man-made chemicals

Emerging constituents is not a new issue

- 47 year history:

1970 1980 1990 2000

1974

NORS

SDWA

Discovery of THMs - (U.S. & Holland)

SOC's created during chlorination of drinking water

Emerging constituents is not a new issue

- 47 year history:
- The Disinfection By-Products Story

1970 1980 1990 2000

1974
Discover THMs

1982
THM Rule

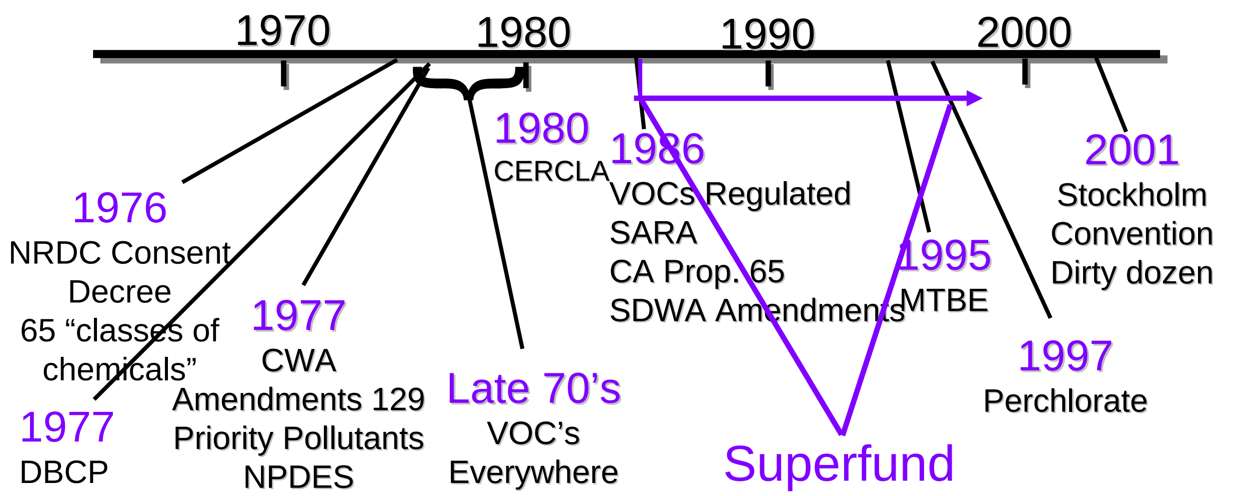
1998
DBP Rule Stage I

2001
NDMA

2006
DBP Rule Stage II

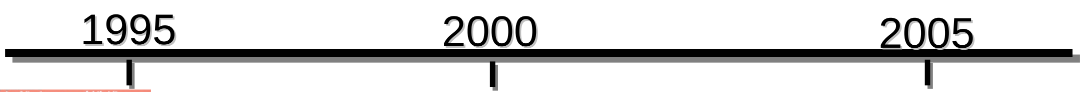
Emerging constituents is not a new issue

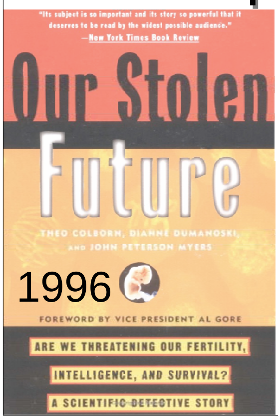
- 47 year history:
- 1977 - Manufactured chemicals: start showing up where they aren't supposed to be



Emerging constituents is not a new issue

- 47 year history:
- Manufactured chemicals: new implications?





Colburn et al., Endocrine Distrupters

A new model for the ecologic impact of chemicals

Emerging constituents is not a new issue

- 47 year history:
- Manufactured chemicals: new implications?

1995 2000 2005

Research has shown pharmaceuticals
-In the environment
-In our water supplies
-In our drinking water

Emerging constituents is not a new issue

- 47 year history:
- Manufactured chemicals: new implications?

1995 2000 2005

As in Rachel Carson's day, this seems to be less an issue for our drinking water supplies and more an issue for the ecological environment that supports us

Emerging constituents is not a new issue

- 47 year history:
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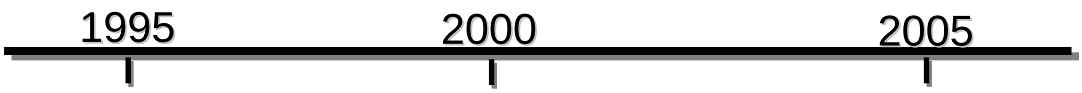


As in Rachel Carson's day, this seems to be less an issue for our drinking water supplies and more an issue for the ecological environment that supports us

But the public is not sanguine

A quick look at today's list

Some Classes of Today’s Emerging Constituents of Concern

- Herbicides (Atrazine, Metolachlor)
- Person care products (DEET, Triclosan)
- Household chemicals (Caffiene, detergents)
- Industrial chemicals (EDTA, Bisphenol a)

Some Classes of Today’s Emerging Constituents of Concern (cont’d)

- Pharmacueticals
  - Metabolic regulators (Diclofenac, Gemfibrozil)
  - Hormone substitutes (EE2)
  - Antibiotics (Sulfamethoxychlor, Erythromycin)
  - Others (Carbazmazepine, Iopromide)
- Microbes (parasites, adenovirus, norovirus)ㄴㄴ
- Nanoparticles

List of 100 Compounds Often Found in U.S. Effluents & Surface Waters

1,4-dichlorobenzene, 1,7-dimethylxanthine, 17α-ethinylestradiol, 17β-estradiol, 2,6-di-*t*-butyl 1.4-benzoquinone, 2,6-di-*t*-butyl phenol, 3-*t*-butyl-4-hydroxy anisole, 4-methyl phenol, 5-methyl-1H-benzotriazole

Acetominophen, Amoxicillin, Androstenedione, Atenolol, Atrazine, Azithromycin, Benzo(a)pyrene, Bezafibrate, Bisphenol-A, Brominated Diphenyl Ether (BDPE), Butylated hydroxyanisole (BHA), Butylated hydroxytoluene (BHT), Caffiene, Carbamazepine, Chloropyrifos, Chlorotetracycline, cholesterol, Ciprofloxacin, Clarithromycin, Clofobric acid, Coprostanol, Cotinine,

DDT, Dehydronifedipine, diatrozate, Diazenon, Diazepam, Di-N-butylphthalate, Diclofenac, Dilantin, Diphenhydrmine, Enroflaxicin, erythromycin, Estriol, Estrone, Ethanol, 2-butoxy-phosphate, Ethinyl Estradiol

Ethylenediamine tetra acetic aid (EDTA), Fluoranthene, Fluoxetine, Galaxolide, Gemfibrozil, Hydrocone, Ibuprofen, Indometacine, Iopromide, Ketrprofen, Lincomycin, Lipitor, Meprobamate, Metolachlor,Methadone, Metroprolol, Monesin, Morphine, Musk Ketone,

Naphthalene, Naproxen, N-N-diethyltoluamide (DEET), Nitrilotriacetate (NTA), Nonylphenol, Nonylphenol poly ethoxylate, Norfloxacin, NDMA, Octylphenol, Octylphenol Poly ethoxylate, Ofloxacin, Oxybenzene,

Pentoxifyline, Phenytoin, Phthalic anhydride, Phenacetine, Polybrominated diphenyl ethers (PBDE), Predisone, Primadone, Progesterone, Propranolol, Pyrene

Roxithromycin, Salicycllic acid, Sulfadimethoxine, Sulfamethazine, Sulfathomethoxazole, Sulfathiozole, TCEP, TCPP, Testosterone, Tonalide, Triclosan, Trimethoprim & Virginiamycin

Of the 100, there are 31 compounds we see or expect to see with some regularity in raw drinking water

Acetominophen, Atenolol, Atrazine, Azithromycin, Bisphenol-A, Caffiene, Carbamazepine, Ciprofloxacin, Erythromycin, Estrone Ethylenediamine tetra acetic aid (EDTA), Galaxolide, Gemfibrozil, Ibuprofen, Iopromide, Meprobamate, Naproxen

N-N-diethyltoluamide (DEET), nonylphenol, nonylphenol polyethoxylate, Phenytoin, Octylphenol, Octylphenol polyethoxylate, Primidone, Sulfamethoxazole, TCEP, Triclosan, & Trimethoprim

Of these 31, *the 11 highlighted in blue* were those most frequently found in recent WRF/SNWA surveys of U.S.tap waters

Acetominophen, *Atenolol*, *Atrazine*, Azithromycin, Bisphenol-A, Caffiene, *Carbamazepine*, Ciprofloxacin, Erythromycin, *Estrone* Ethylenediamine tetra acetic aid (EDTA), Galaxolide, *Gemfibrozil*, Ibuprofen, Iopromide, *Meprobamate*, *Naproxen*

N-N-diethyltoluamide (DEET), nonylphenol, nonylphenol polyethoxylate, *Phenytoin*, Octylphenol, Octylphenol polyethoxylate, Primidone, *Sulfamethoxazole*, *TCEP*, Triclosan, & *Trimethoprim*

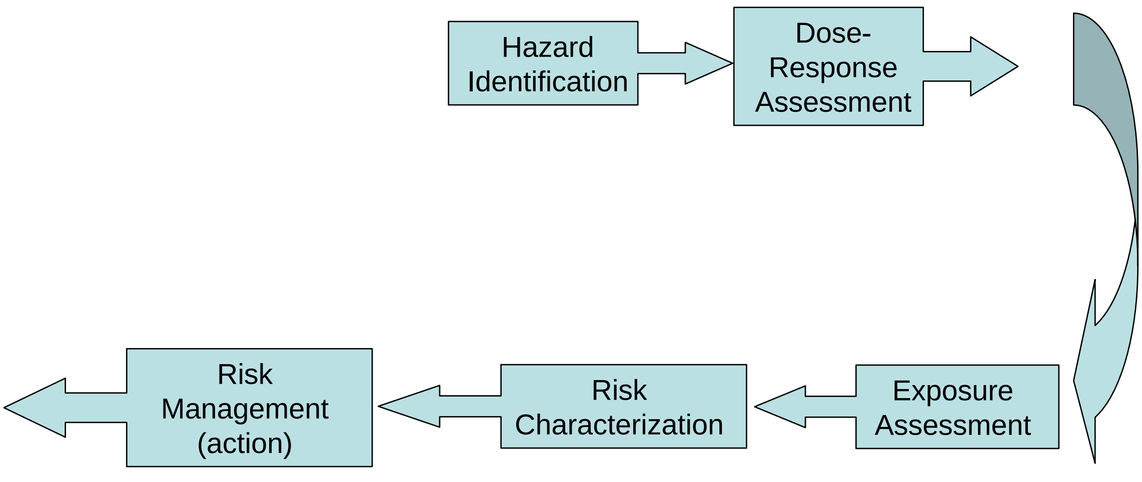
Of the 31, there are also 13 compounds that are particularly persistent (candidates in groundwater)

Acetominophen, Atenolol, Atrazine, Azithromycin, *Bisphenol-A*, Caffiene, *Carbamazepine*, Ciprofloxacin, Erythromycin, Estrone *Ethylenediamine tetra acetic aid (EDTA)*, Galaxolide, *Gemfibrozil*, Ibuprofen, *Iopromide*, *Meprobamat*e, Naproxen

N-N-diethyltoluamide (DEET), *nonylphenol, nonylphenol polyethoxylate, Phenytoin, Octylphenol, Octylphenol* polyethoxylate, Primidone, Sulfamethoxazole, TCEP, Triclosan, & Trimethoprim

So how do we manage this issue?

The Current U.S. Model Follows the Advice of the NRC in the 1980s



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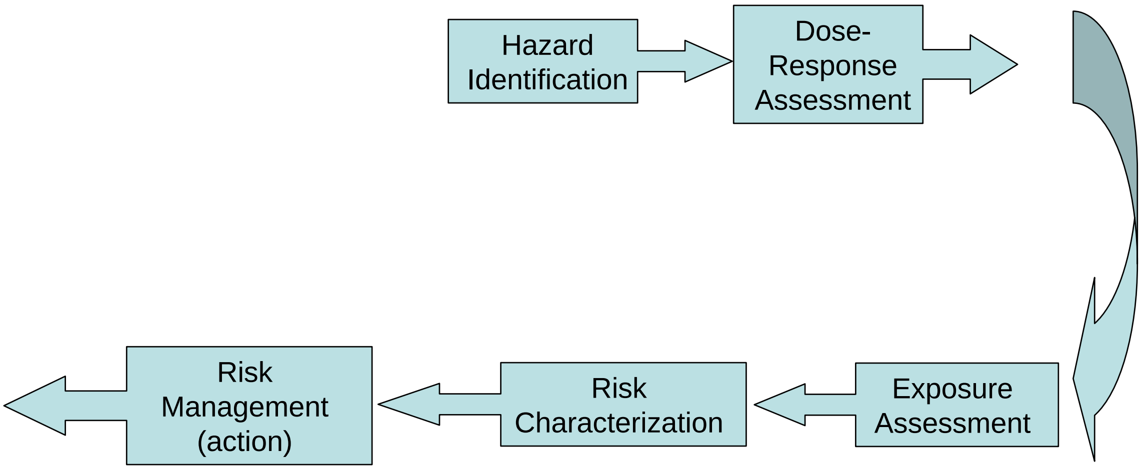
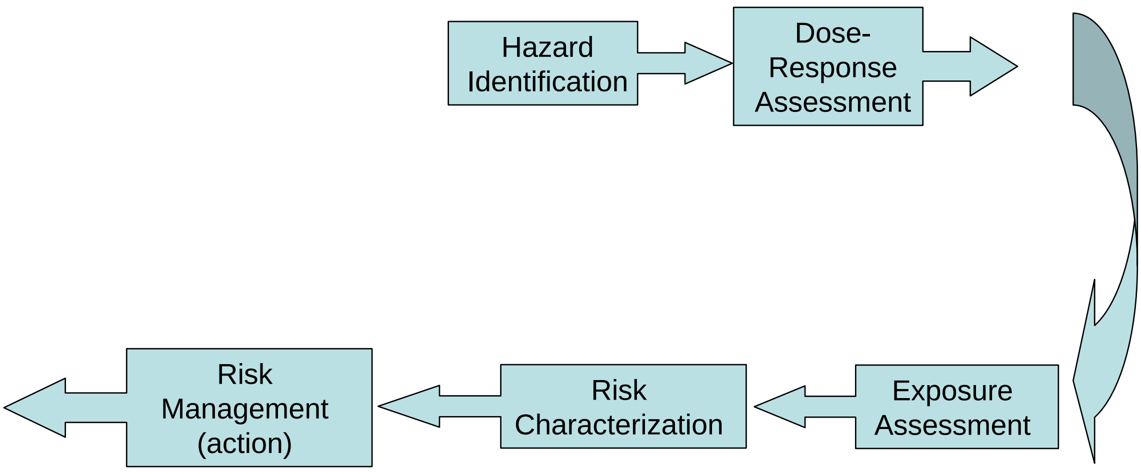


- To use this process we have to get data:
  - Dose-response
  - Occurrence

The Current U.S. Model Follows the Advice of the NRC in the 1980s



- Note: Risk management is the last step

But problems have developed in the NRC Risk Management Process

- Hard, scientific data are not available (and won't be)
  - We chose not to directly measure health-effects in humans
    - So we test outcomes in other animals
  - We cannot observe effects at low doses
    - So we give the animals high doses
  - And we use cross-species safety factors and multi-stage models to understand what the results mean
    - both are logical, neither can be verified
  - We suspect that impacts resulting from exposure to one chemical may be affected by exposure to another
    - but we don't understand these complexities well enough to include them in our risk assessments

But problems have developed in the NRC Risk Management Process

- Most of the analytical methods we use to assess occurrence are target-specific
  - i.e. we only find what we look for
  - Hence, we don't know what we don't know
- The analytical methods we do have are becoming increasingly sensitive
  - Increasingly we know something is present without knowing if its presence, at that level, is significant

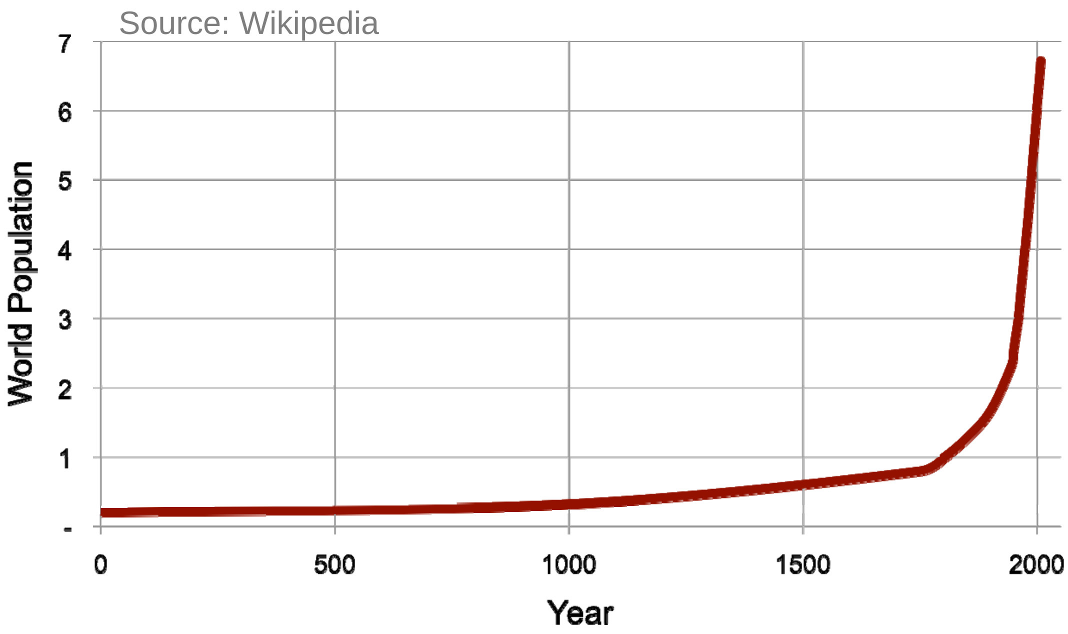
But problems have developed in the NRC Risk Management Process

- It is not surprising that disagreements exist among members of the scientific community about how the data we do have should be interpreted
- Nor is it surprising that people don't agree about the significance of the risks identified
- The problem is even more complex when we expand our horizon to consider impacts on the entire eco-sysytem

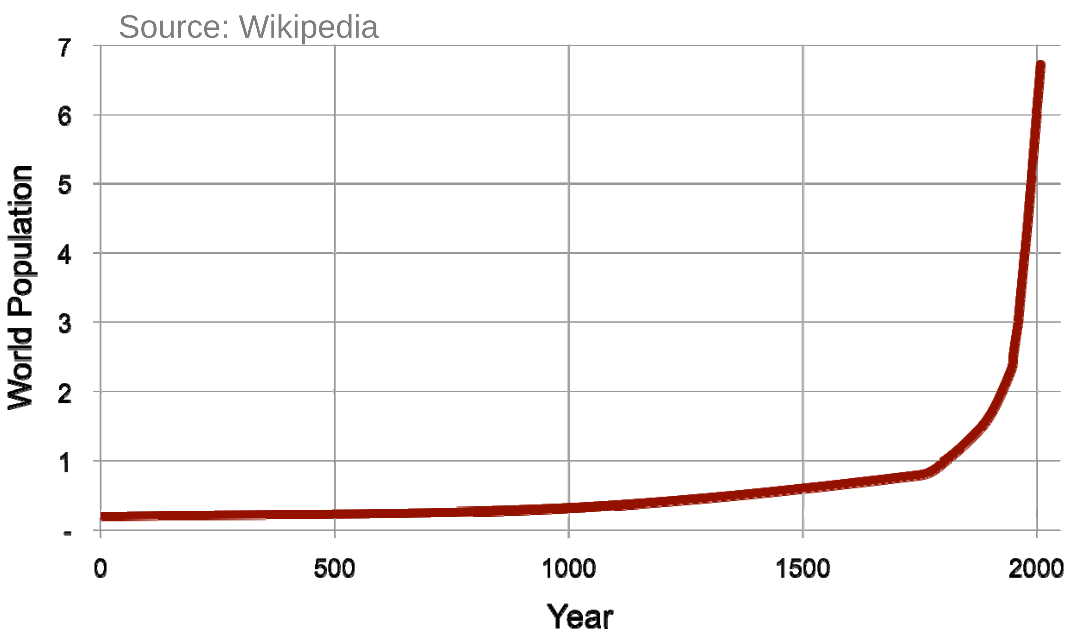
But problems have developed in the NRC Risk Management Process

- Change is coming at an increasingly rapid pace
  - Driven by population growth
  - Driven by economic growth
- Potential new problems are out-stripping the resources we have to address them

A Plot of the World's Population Illustrates the Pace of Change



But the increase during my lifetime has been particularly profound



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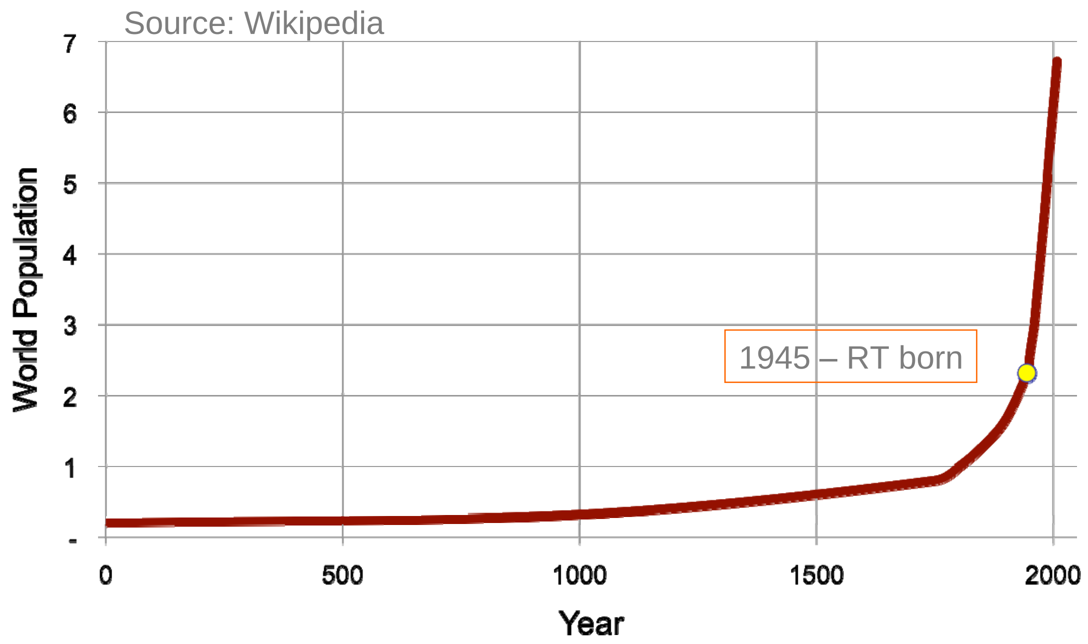

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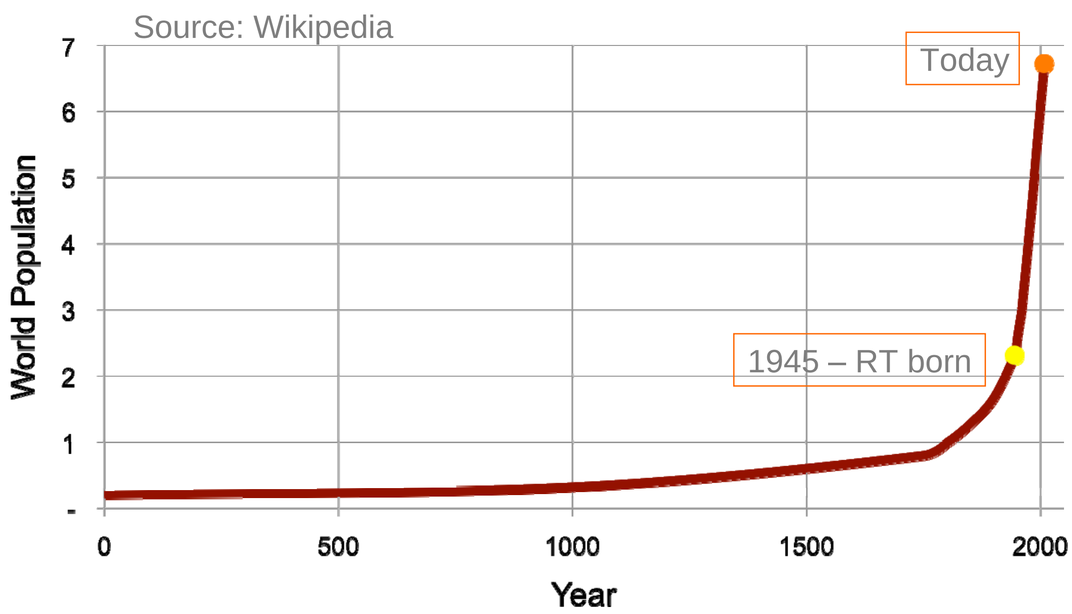

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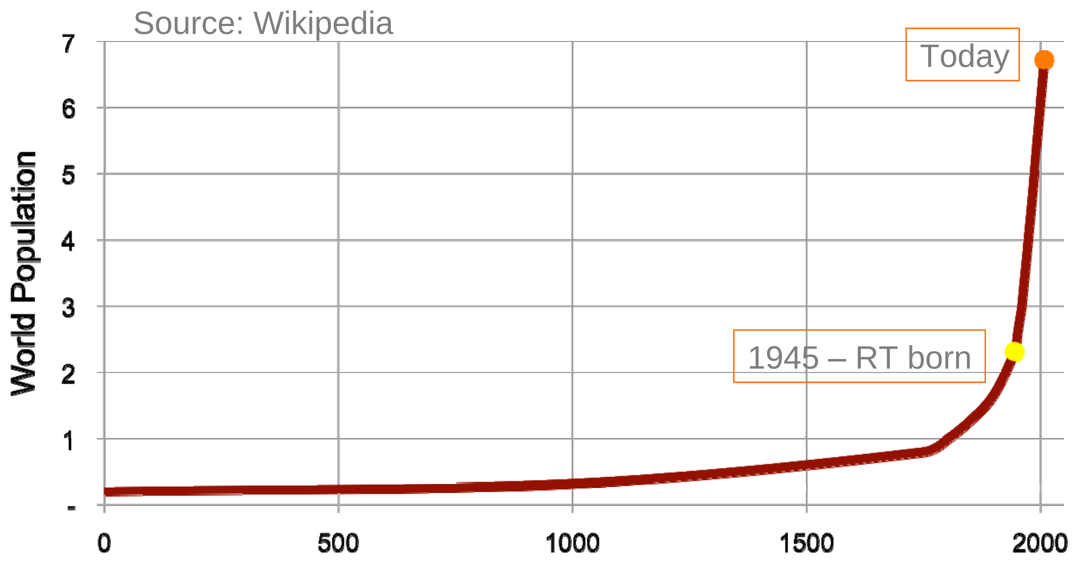
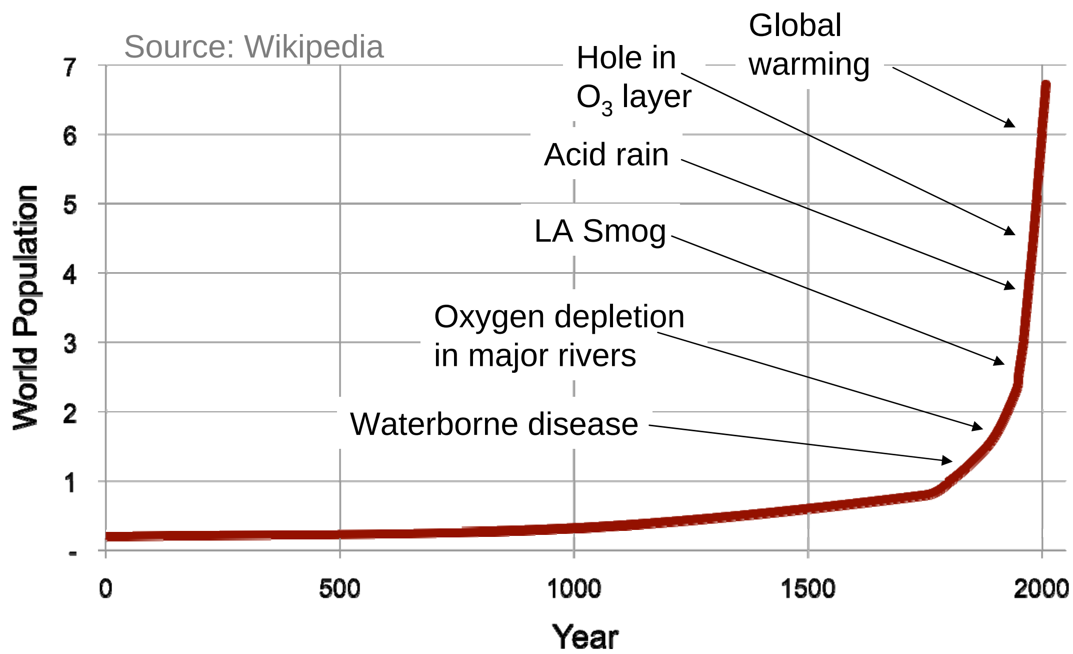


Driven by technological innovation the world economy has grown faster yet

As the Scale of Man's Activities Have Increased, The Scale of their Impact Has Increased as well



We need a new scheme

- It is time we (the U.S.) re-examined our approach
- A dialogue about the proper design of preventative action may be the right place to start (early moves in risk management)
- Possible guidelines for precaution
  - Substance is known to be toxic
  - Evidence of adverse effects is accumulating
  - Substance is not removed by secondary treatment
  - Substance is persistent in the environment
  - Substance accumulates in the food chain

How might this work?

Elements of an Appropriate Response

1. Essential tenant: On-going investment is required (no illusion that the “problem” will soon be “solved”)
2. Monitor Monitor, Monitor
   – Develop & maintain lists of compounds
   – Develop & maintain standard methods of analysis
   – Conduct regular national surveys
   – On-going requirements for monitoring by water and wastewater utilities and industry (effluents, influents, groundwater, biota)

Elements of an Appropriate Response

3. Cradle to grave management
   – National program on habits of disposal
   – On-going research on removal in water and wastewater treatment
   – Upgrade treatment when affordable (both water & wastewater)
4. Find the Bad Actors and Fix them
   – Identify compounds that: persist in the environment, accumulate in the biota, are resistant to treatment, show evidence of toxicity, etc.
   – Study their toxicity
   – Find replacements for problem compounds

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