TOXIC SUBSTANCES IN THE ENVIRONMENT

IPOL 8512



Key Types of Toxic Substances

Heavy Metals

- Lead (Pb)
- Mercury (Hg)
- Cadmium (Cd)
- Chromium (Cr)

Other Elements

- Arsenic (As)
- Beryllium (Be)

Organic Chemicals

- Halogenated hydrocarbons
- PCBs
- Dioxin
- Furans
- Pthalates

Air Pollutants

- SO_X
- NO_X
- Volatile Organic Compounds (VOCs)
- ozone
- particulate matter (PM)

Radiation

- radioactive substances
- other radiation sources

Lead Poisoning

- Lead is toxic to many organs and tissues including the heart, bones, intestines, kidneys, and reproductive and nervous systems.
- The primary cause of lead's toxicity is its interference with a variety of enzymes.
- Lead interferes with the release of neurotransmitters, chemicals used by neurons to send signals to other cells.
- Particularly toxic to children, causing potentially permanent learning and behavior disorders.
- The half-life of lead is measured in weeks for blood, months for soft tissues, and years for bone.

http://en.wikipedia.org/wiki/Lead_poisoning

Lead in Paint

- As a pigment,
 - lead(II) chromate, PbCrO₄, chrome yellow
 - lead(II) carbonate, PbCO₃, white lead
- Speed up drying
- Increase durability
- Maintain a fresh appearance
- Resist moisture that causes corrosion.
- Still used in some countries, but banned in the U.S. and the U.K.

Tetraethyllead, (CH₃CH₂)₂Pb

- Added to gasoline beginning in the 1920s as an inexpensive octane booster that allowed engine compression to be raised substantially, which in turn increased vehicle performance and fuel economy.
- TEL was phased out starting in the US in the mid-1970s because of its neurotoxicity and its deleterious effect on catalytic converters.
- It is still used as an additive in aviation fuel for piston engine-powered aircraft.





http://en.wikipedia.org/wiki/Tetraethyllead

Ways to Describe Organic Compounds

Lewis structures



 Condensed Formulas CH₃CH(CH₃)CH₃

Line Drawings

Alkanes - Hydrocarbons (compounds composed of carbon and hydrogen) in which all of the carbon-carbon bonds are single bonds



2,2,4-trimethylpentane, CH₃C(CH₃)₂CH₂CH(CH₃)CH₃

Pre-ignition Knock and Octane Rating



If the gasoline-air mixture ignites too soon, before the peak of the stroke of the piston, the piston pushes the crankshaft in the opposite direction, causing a vibration or "pre-ignition knock".

If the gasoline-air mixture ignites at (or just past) the peak of the stroke of the piston, the crankshaft is turned, which ultimately turns the wheels.

Straight-chain hydrocarbons are more likely to pre-ignite, so a gasoline that has a high percentage of straight-chain hydrocarbons has a low octane rating.

Branched-chain hydrocarbons are less likely to pre-ignite, so a gasoline that has a high percentage of branched-chain hydrocarbons has a high octane rating.

Steps to Octane Rating

- Measure efficiency and degree of vibration for a test engine running on various percentages of heptane (a straight-chain hydrocarbon) and 2,2,4-trimethylpentane (a branched-chain hydrocarbon).
- Run the same test engine with the gasoline to be tested, and measure its efficiency and degree of vibration.
- Assign an octane rating to the gasoline based on comparison of the efficiency and degree of vibration of the test engine with the gasoline and the various percentages of 2,2,4-trimethylpentane (octane or isooctane) and heptane. For example, if the gasoline runs the test engine as efficiently as 91% 2,2,4-trimethylpentane (octane or isooctane) and 9% heptane, it gets an octane rating of 91.

Mercury Poisoning

- The consumption of fish is by far the most significant source of ingestion-related mercury exposure in humans and animals, although plants and livestock also contain mercury due to bioaccumulation of mercury from soil, water and atmosphere.
- An estimated two-thirds of human-generated mercury comes from stationary combustion, mostly of coal.
- Mercury is highly reactive with selenium, an essential dietary element required by about 25 genetically distinct enzyme types (selenoenzymes). Among their numerous functions, selenoenzymes prevent and reverse oxidative damage in the brain.

http://en.wikipedia.org/wiki/Mercury_poisoning

Heavy Metal Poisoning Treatment

- Chelation therapy

 metal ions, such
 as lead or mercury
 ions trapped in the
 center of the
 chelating agent.
- The chelate is nontoxic and can be excreted in the urine.



Arsenic Poisoning

- A 2007 study found that over 137 million people in more than 70 countries are probably affected by arsenic poisoning from drinking water.
- Non-cancer effects can include thickening and discoloration of the skin, stomach pain, nausea, vomiting; diarrhea; numbness in hands and feet; partial paralysis; and blindness.
- Arsenic has been linked to cancer of the bladder, lungs, skin, kidney, nasal passages, liver, and prostate.
- EPA has set the arsenic standard for drinking water at .010 parts per million (10 parts per billion) to protect consumers served by public water systems from the effects of long-term, chronic exposure to arsenic.

Arsenic Poisoning

- Arsenic and some heavy metals act by chemically reacting with adjacent thiol residues on metabolic enzymes, creating a chelate complex that inhibits the affected enzyme's activity.
- Dimercaprol, which is a chelating agent that is used to treat arsenic and heavy metal poisoning, competes with the thiol groups for binding the metal ion, which is then excreted in the urine.



http://en.wikipedia.org/wiki/Arsenic_poisoning

Polychlorinated Biphenyls (PCBs)

 Organochlorides with 2 to 10 chlorine atoms attached to biphenyl, which is a molecule composed of two benzene rings.



- Used as a dielectric (an electrical insulator that can be polarized by an applied electric field) and coolant fluids in transformers, capacitors, and electric motors.
- According to the EPA, PCBs have been shown to cause cancer in animals, and there is also evidence that they can cause cancer in humans.

Furans

• Furan is a heterocyclic organic compound, consisting of a five-membered ring with four carbon atoms and one oxygen.



- The class of compounds containing such rings are also referred to as furans.
- Byproducts of the production of other chemicals, such as herbicides.
- It is toxic and may be carcinogenic.
- Furan is used as a starting point to other specialty chemicals.

Pthalates

• Phthalates are esters of phthalic acid.



- Mainly used as plasticizers (substances added to plastics to increase their flexibility, transparency, durability, and longevity).
- Used primarily to soften polyvinyl chloride (PVC).
- Being phased out of many products in the United States, Canada, and European Union over health concerns.
- Affect the endocrine system in studies of rodents exposed to certain phthalates, high doses have been shown to change hormone levels and cause birth defects.





The R' must be a hydrocarbon group. It cannot be a hydrogen atom.



Ethyl butanoate, CH₃CH₂CH₂CO₂CH₂CH₃

Endocrine System

The **endocrine system** is the system of glands, each of which secretes different types of hormones.



Dioxins

• **2,3,7,8-Tetrachlorodibenzo***-p***-dioxin** (**TCDD**) is usually formed as a side product in organic synthesis and burning.



- TCDD is the most potent compound of the dioxins
- A contaminant in Agent Orange, a herbicide used in the Vietnam War
- TCDD is a carcinogen.
- With an LD₅₀ of only 20 µg/kg in rats, TCDD is one of the most toxic man-made substances.

Volatile Organic Compounds (VOCs)

- Organic chemicals that readily evaporate or sublime and enter the surrounding air.
- Not counting methane, biological sources emit an estimated 1150 teragrams of carbon per year in the form of VOCs. The majority of VOCs are produced by plants, the main compound being isoprene, CH₂C(CH₃)CHCH₂.



- Hydrocarbons, ethyl acetate, glycol ethers, and acetone from paint.
- Tetrachloroethene is used widely in dry cleaning and by industry.

http://en.wikipedia.org/wiki/Volatile_organic_compound

Volatile Organic Compounds (VOCs)

- Benzene, C₆H₆, (a known human carcinogen) is found in environmental tobacco smoke, stored fuels, and exhaust from cars. Benzene also has natural sources such as volcanoes and forest fires.
- Perchloroethylene. C₂Cl₄, is used mostly in dry cleaning. It has been linked to cancer in animals. It is also suspected to cause many of the breathing related symptoms of exposure to VOC's.
- Methylene chloride, CH₂Cl₂, can be found in adhesive removers and aerosol spray paints, and it has been proven to cause cancer in animals. In the human body, methylene chloride is converted to carbon monoxide, causing the same symptoms as exposure to carbon monoxide.

IRIS WEB SITE

IRIS = Integrated Risk Information System = official EPA web site on health effects of toxic substances in the environment

http://www.epa.gov/iris/

Human Toxome Project

- Just as scientists raced to define the human genome, the Human Toxome Project (HTP) at Environmental Working Group is working to define the human toxome-the full scope of industrial pollution in humanity.
- HTP scientists use cutting edge biomonitoring techniques to test for industrial chemicals like bisphenol A and perchlorate that enter the body through pollution or even as ingredients in everyday consumer products.

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Substances Tested for in EWG Study



PCBs — Industrial insulators and lubricants. Banned in the U.S. in PCB 1976. Persist for decades in the environment. Accumulate up the

food chain, to man. Cause cancer and nervous system problems.

Dioxins — Pollutants, byproducts of PVC production, Diox industrial bleaching, and incineration. Cause cancer in man. Persist for decades in the environment. Very toxic to developing endocrine (hormone) system.



Furans - Pollutants, byproducts of plastics production, -ur industrial bleaching and incineration. Expected to cause cancer in man. Persist for decades in the

environment. Very toxic to developing endocrine (hormone) system.



Metals — Lead, mercury, arsenic and cadmium - Cause lowered IQ, developmental delays, behavioral disorders and cancer at doses found in the environment. For lead, most exposures are from lead paint. For mercury, most exposures are from canned tuna. For arsenic, most exposures are from arsenic (CCA) treated lumber and contaminated drinking water. For cadmium, sources of exposure include pigments and bakeware.



Organochlorine insecticides. DDT, chlordane and other pesticides. Largely banned in the U.S. Persist for decades in the environment. Accumulate up the food chain, to man. Cause cancer and numerous reproductive effects.



Organophosphate insecticide metabolites — Breakdown products of chlorpyrifos, malathion and others. Potent nervous system toxicants. Most common source of exposure is residues in food. Recently banned for indoor uses.



Phthalates — Plasticizers. Cause birth defects of male Pht reproductive organs. Found in a wide range of cosmetic and personal care products. Some phthalates recently banned in Europe.



Volatile and Semi-volatile organic chemicals. -

SNoc Industrial solvents and gasoline ingredients like xylene and ethyl benzene. Toxic to nervous system, some

heavily used SVOCs (benzene) cause cancer.

Participant: Sharyle Patton Found 92.6166666666667-109 of 214 tested chemicals



Sharyle Patton's blood and urine contained 92.6166666666667-109 of 214 industrial compounds, pollutants and other chemicals tested, including chemicals linked to immune system toxicity, brain and nervous system toxicity, and birth defects and developmental delays.

• This participant's samples show above average levels of <u>Polychlorinated</u> <u>biphenyls (PCBs)</u>, <u>Chlorinated dioxins & furans</u>, <u>Methylmercury</u> and <u>Lead</u> compared to all others in EWG studies

Summary of chemicals found in Sharyle Patton

CHEMICAL FAMILY	LEVEL FOUND	HEALTH EFFECTS	EXPOSURE ROUTES
<u>Alkylphenols</u>	found, not quantified	Endocrine system	Cosmetics, detergents, pesticides, paints, carpet and dry cleaning
<u>Chlorinated dioxins &</u> <u>furans</u>	high	Immune system (including sensitization and allergies), Birth defects and developmental delays	Dietary sources, fatty meat, dairy and fish
Lead	moderate		Lead-based paint in older homes, household dust, vinyl products, tap water
Methylmercury	high		Dietary sources, particularly seafood
<u>Organochlorine</u> <u>Pesticides (OCs)</u>	low	Reproduction and fertility	Contaminated food and drinking water
<u>Organophosphate</u> <u>Pesticide metabolites</u>	moderate	Brain and nervous system	Contaminated food and drinking water

ABOUT THIS PARTICIPANT:

Sharyle Patton, an organizer from Bolinas, CA, participated in the 2003 biomonitoring investigation entitled "EWG/Commonweal Study #1, industrial chemicals and pesticides in adults." She gave blood and urine for the study at age 58.

Sharyle Patton is co-director of the Collaborative on Health and Environment, a group of individuals and organizations interested in linkages between environment and health. She was previously the northern co-chair of the International Persistent Organic Pollutants (POPS) Elimination Network, a network of over 350 non-governmental organizations around the world which worked successfully for the positive conclusion of the UN treaty on POPS, signed in May 2001. She has been active in UN conferences on women's reproductive health and sexual rights issues.

Related links:

<u>Report executive</u>
 <u>summary</u>

Location:

Bolinas, CA

Participant's groups: <u>Patton Lerner Family</u>, <u>Female</u>, <u>Commonweal</u>, <u>Adult</u>

Study:

EWG/Commonweal Study #1, industrial chemicals and pesticides in adults

HEALTH & SAFETY CONCERNS:	chemicals found in this person
Immune system	1

http://www.ewg.org/sites/humantoxome/participants/participant.php?subject=bb1_sub6

Number of chemicals found in 9 people tested that are linked to the listed health impact Range Health Effect or Body System (lowest and Affected Average Total found highest number found in all 9 number in 9 people people found in all 9 people) 76 [2] cancer [1] 53 36 to 65 birth defects / developmental 55 79 [3] 37 to 68 delays 5 11 [4] 4 to 7 vision 58 86 [5] hormone system 40 to 71 59 84 [6] stomach or intestines 41 to 72 kidney 54 80 [7] 37 to 67 62 46 to 73 brain, nervous system 94 [8] 77 [9] reproductive system 55 37 to 68 55 38 to 67 lungs/breathing 82 [10] 56 84 [11] 37 to 70 skin 42 69 [12] 26 to 54 liver cardiovascular system or blood 82 [13] 55 37 to 68 hearing 34 50 [14] 16 to 47 35 to 65 immune system 53 77 [15] male reproductive system 47 70 [16] 28 to 60 female reproductive system 42 61 [17] 24 to 56

TABLE 1: The chemicals we found are linked to serious health problems

Persistent Organic Pollutants

- Remain intact for exceptionally long periods of time (many years)
- Become widely distributed throughout the environment as a result of natural processes involving soil, water and, most notably, air
- Accumulate in the fatty tissue of living organisms including humans, and are found at higher concentrations at higher levels in the food chain
- Are toxic to both humans and wildlife.

- Stockholm Convention on Persistent Organic Pollutants (POPs)
 - Adopted in 2001 and entered into force in 2004
 - Requires Parties to take measures to eliminate or reduce the release of POPs into the environment.
 - The Convention is administered by the United Nations Environment Programme and is based in Geneva, Switzerland.
 - A global treaty to protect human health and the environment from chemicals that remain intact in the environment for long periods, become widely distributed geographically, accumulate in the fatty tissue of humans and wildlife, and have adverse effects to human health or to the environment.

- Stockholm Convention on Persistent Organic Pollutants (POPs)
 - Exposure to Persistent Organic Pollutants (POPs) can lead serious health effects including certain cancers, birth defects, dysfunctional immune and reproductive systems, greater susceptibility to disease and even diminished intelligence.
 - Given their long range transport, no one government acting alone can protect is citizens or its environment from POPs.

 Aldrin – Elimination - an organochlorine insecticide that was widely used until the 1970s

CI

 Chlordane – elimination - an organochlorine compound used as a pesticide.

• Dieldrin – elimination – an insecticide

CI

....C

• Endrin – elimination – an insecticide

Heptachlor – elimination – an insecticide

Hexachlorobenzene – elimination – a fungicide



CI'''

Cln

 CH_3

 CH_3

• Mirex – elimination – an insecticide

- Toxiphene elimination an insecticide
- DDT restriction insecticide banned for CH₂ agricultural use worldwide under the Stockholm Convention, but limited use in disease vector control allowed, e.g. permits the public health use for the control of mosquitoes (the malaria vector)

 Polychlorinated Biphenyls – elimination - 209 configurations of organochlorides with 2 to 10 chlorine atoms attached to biphenyl, which is a molecule composed of two benzene rings. 3 2 2' 3'



- Used as dielectric (an electrical insulator that can be polarized by an applied electric field) and coolant fluids in transformers, capacitors, and electric motors.
- PCB production was banned by the United States Congress in 1979 and by the Stockholm Convention on Persistent Organic Pollutants in 2001.
- According to the EPA, PCBs have been shown to cause cancer in animals, and there is also evidence that they can cause cancer in humans.

Polychlorinated dibenzodioxins (PCDDs or dioxins) –



- May cause developmental disturbances and cancer.
- Occur as by-products in the manufacture of some organochlorines, in the incineration of chlorinecontaining substances such as PVC (polyvinyl chloride), in the chlorine bleaching of paper, and from natural sources such as volcanoes and forest fires.

http://en.wikipedia.org/wiki/Stockholm_Convention_on_Persistent_Organic_Pollutants

α-Hexachlorocyclohexane – elimination - byproduct of • the production of the insecticide lindane Chlordecone – elimination – insecticide Polybrominated biphenyls (PBBs) - elimination \bullet - flame retardants 2

http://chm.pops.int/Convention/ThePOPs/TheNewPOPs/tabid/2511/Default.aspx

6'

(Br)

 $(Br)_x$
Stockholm Convention POPs

Br_m

CI

Brn

Cl

 Polybrominated diphenyl ethers or PBDEs – elimination - flame retardants

 Lindane – elimination - insecticide and as a pharmaceutical treatment for lice and scabies

Pentachlorobenzene - elimination

http://chm.pops.int/Convention/ThePOPs/TheNewPOPs/tabid/2511/Default.aspx

Stockholm Convention POPs

 Perfluorooctanesulfonic acid or perfluorooctane sulfonate (PFOS) – restricted - key ingredient in Scotchgard, a fabric protector made by 3M, and numerous stain repellents



More to come

http://chm.pops.int/Convention/ThePOPs/TheNewPOPs/tabid/2511/Default.aspx

U.S. Chemical Industry

- One of the United States' largest manufacturing industries,
- One of the top exporting sectors of U.S. manufacturing.
- Accounting for 19 percent of global production, the United States is the world's leading chemicals producer and the world's second largest exporter of chemicals.
- 10,000 firms
- Produce more than 70,000 products.
- In 2009, the chemicals industry had revenues of \$674 billion
- Directly employed more than 800,000 U.S. workers, with additional indirect employment of more than 790,000 by industry suppliers.
- Investment of \$49 billion in research and development in 2009, and a commitment to the advancement of chemicals technologies, the U.S. chemicals industry is responsible for one out of every nine patents filed in the United States.

http://selectusa.commerce.gov/about-selectusa

U.S. Chemical Industry

- <u>Basic Chemicals</u>: These include organic and inorganic chemicals, synthetic polymers (plastics), dyes and pigments. Polymers, in particular, have experienced significant growth as a replacement for traditional materials in the automotive, construction and packaging end-use markets.
- <u>Specialty Chemicals</u>: These include adhesives and sealants, water treatment chemicals, plastic additives, catalysts and coatings.
- <u>Agricultural Chemicals</u>: These play a crucial role in the farm economy and the food processing sector. Thanks to modern agriculture, farmers have doubled the production of world food supplies since 1960, tripled the output of foods such as cooking oils and meats, and increased per capita food supplies in the developing world by 25 percent.

U.S. Chemical Industry

- <u>Pharmaceuticals</u>: These include diagnostics, prescription drugs, vaccines, vitamins, and over-the-counter drugs for human and veterinary applications. This subsector also includes biotechnology products.
- <u>Consumer Products</u>: These include soaps, detergents and cleaners, as well as toiletries and cosmetics.

The U.S. Chemical Industry

- The federal government registers an average of 2,000 newly synthesized chemicals each year → 7 per day
- 8 of 10 new chemicals win approval in less than 3 weeks
- 5,000 different chemical ingredients in cosmetics
- 3,200 different chemicals added to food
- 1,000 different chemicals used in 12,000 consumer products
- 500 different chemicals used as active ingredients in pesticides
- U.S. industrial production = 3 × 10¹² kg of 9,000 different chemicals (EPA 2001) ≈ 10,000 kg for each American per year

Toxic Substances Control Act (TSCA)

- Passed by the United States Congress in 1976
- Regulates the introduction of new or already existing chemicals.
- It grandfathered most existing chemicals, in contrast to the Registration, Evaluation and Authorization of Chemicals (REACH) legislation of the European Union.
- Does not separate chemicals into categories of toxic and non-toxic.
- It prohibits the manufacture or importation of chemicals that are not on the TSCA Inventory (or subject to one of many exemptions).

http://en.wikipedia.org/wiki/Toxic_Substances_Control_Act

Toxic Substances Control Act (TSCA)

- Chemicals that are listed on the TSCA Inventory are referred to as "existing chemicals". Chemicals not listed are referred to as new chemicals.
- Manufacturers must submit notification to the U.S. Environmental Protection Agency (EPA) prior to manufacturing (or importing) new chemicals for commercial purposes.
- There are notable exceptions, including one for research and development, and for substances regulated under other statutes.
- New chemical notifications are reviewed by the agency and if the agency finds an "unreasonable risk to human health or the environment," it may regulate the substance in a variety of ways, from limiting uses or production volume to outright banning them.

http://en.wikipedia.org/wiki/Toxic_Substances_Control_Act

Bhopal Incident

- One of the world's worst industrial disasters
- December 2,3 1984 at the Union Carbide India Limited (UCIL) pesticide plant in Bhopal, Madhya Pradesh.
- Around 42,000 kilograms (93,000 lb) of methyl isocyanate and other gases were released, exposing over 500,000 people.
- The official immediate death toll was 2,259.
- The government of Madhya Pradesh confirmed a total of 3,787 deaths related to the gas release.
- Others estimate 8,000 died within two weeks and another 8,000 or more have since died from gas-related diseases.
- A government affidavit in 2006 stated the leak caused 558,125 injuries including 38,478 temporary partial and approximately 3,900 severely and permanently disabling injuries.

http://en.wikipedia.org/wiki/Bhopal_disaster

Bhopal Incident - Methyl Isocyanate, CH₃NCO

- An intermediate chemical in the production of carbamate pesticides, such as carbaryl. (See next slide.)
- Highly toxic and irritating material, it is hazardous to human health.
- Exposure symptoms includes coughing, chest pain, irritation of the eyes, nose and throat, as well as skin damage.
- Higher levels of exposure, over 21 ppm, can result in pulmonary or lung edema, emphysema and hemorrhages, bronchial pneumonia and death.
- The gas cloud may have also contained phosgene, hydrogen cyanide, carbon monoxide, hydrogen chloride, oxides of nitrogen, monomethyl amine (MMA) and carbon dioxide.

http://en.wikipedia.org/wiki/Bhopal_disaster

Bhopal Incident



 Methylamine (1) reacts with phosgene (2) producing methyl isocyanate (3) which reacts with 1-naphthol (4) to yield carbaryl (5)

http://en.wikipedia.org/wiki/Bhopal_disaster

Toxic Release Inventory

- TRI created by Emergency Planning and Community Right-to-Know Act of 1986 (EPCRA), expanded by Pollution Prevention Act of 1990 (PPA)
- TRI = U.S. database of annual toxic emissions by ~23,000 industrial and government facilities
- "toxic" defined by a list containing ~650 chemical substances
- Purposes: public right to know, tracking emissions trends over time, awareness of responsibility

Toxic Release Inventory Limitations

- Does not regulate
- Does not assess toxic risk
- Reports only pounds of materials released
- Not all facilities report
- Not all substances are reported
- Often based on estimates rather than measurements

- From 2009-2010 disposal or other releases increased by 16%
- Opposite downward trend since 2006 (decrease from 2008-2009 was 13%)
- Many but not all industries show an increase
- Facilities reporting to TRI down by 2%







SEPA Long-Term Trends of Releases by Media



 Since 2004, the percentage of air releases has been decreasing while the percentage of land disposal has been increasing.



2009 and 2010 TRI Releases by Media

- Total on-site disposal or other releases up 16% (about 540 million lbs)
 - Air releases down 6% (about 58 million lbs)
 - Surface water discharge up 9% (about 19 million lbs)
 - Land up 28% (about 478 million lbs)
 - Underground injection up 27% (about 48 million lbs)
- Total off-site disposal or other releases up 15% (about 53 million lbs)



€EPA

2009 – 2010 Data by Sectors

- Change in total disposal or other releases, 2009-2010, for sectors with largest total releases
 - Metal mines increased 487 million lbs (43%)
 - Chemical manufacturing increased 83 million lbs (19%)
 - Primary Metals increased 63 million lbs (20%)
 - Paper increased 2.6 million lbs (1%)

- Electric utilities decreased 100 million lbs (12%)
- Food/beverages decreased 622,000
 lbs (less than 1%)







A Closer Look at Facilities with Large Increases and Decreases

- Largest increasers for releases overall
 - Four metal mining facilities (+510 million lbs)
 - Possible reasons:
 - · Amount and composition of ore changes year to year
 - Improved sampling method
 - No longer eligible for the *de minimis* exemption for reporting certain chemicals
- Largest decreasers for releases in electric utilities sector
 - Four largest decreasing electric utilities (- 68 million lbs)
 - Possible reasons:
 - Improved estimation method
 - Improved pollution control
 - Changes in composition of coal



Releases of Persistent Bioaccumulative and Toxic chemicals (PBTs)

- PBTs are of particular concern
 - Because of persistence, bioaccumulative nature and high toxicity
 - Typically released at lower quantities
 - Have lower TRI reporting thresholds
- 2010 data for PBTs
 - Lead and lead compounds increased 51% from 2009-2010, mostly metal mining land disposal
 - Mercury and mercury compounds down 20%
 - Overall, 2010 mercury and mercury compound releases for the electric utilities sector went up by about 9% (11,706 lbs) over 2009 reporting. For this sector, however, 2010 air releases for mercury went down by about 6% compared to 2009, but were offset by larger increases in releases to land both on-site and off-site.
 - Polycyclic aromatic carbons (PACs) up 30%
 - Polychlorinated biphenyls (PCBs) up 23%
 - Dioxin and dioxin-like compounds (measured in grams) up 18%



Economic Analysis

- Comparing releases to production measures
 - Manufacturing sector
 - Releases decreased 29%, but production increased 4% since 2001
 - · Releases have decreased despite growth in production
 - Metal mining sector
 - Releases decreased 29%, while production decreased only 16% since 2001
 - Analysis suggests factors other than production play a big role in reducing TRI releases
 - Electric utilities sector
 - Releases decreased 34%, while production decreased only 7% since 2001
 - Analysis suggests factors other than production play a big role in reducing TRI releases
 - Decreases in reported mercury emissions, specifically, may be due to changes in reporting, economic conditions, changes in the way utilities operate, and/or responses to federal and state actions such as state guidelines or rules, federal rules, or enforcement actions.
 - See appendices for more details

Other Chemical Regulations

- In the United States, new pharmaceutical products must be approved by the Food and Drug Administration (FDA) as being both safe and effective.
- The United States Federal Food, Drug, and Cosmetic Act is a set of laws passed by Congress in 1938 giving authority to the U.S. Food and Drug Administration (FDA) to oversee the safety of food, drugs, and cosmetics.
- Pesticide regulation in the United States is primarily a responsibility of the Environmental Protection Agency.
 - The Federal Insecticide, Fungicide, and Rodenticide
 Act (FIFRA) is a United States federal law that set up
 the basic U.S. system of pesticide regulation to protect
 applicators, consumers, and the environment.

- Basel Convention The Basel Convention on the Control of Transboundary Movements of Hazardous Wastes and their Disposal is
 - a global environmental agreement on hazardous and other wastes.
 - It came into force in 1992.
 - The Convention has 172 Parties and aims to protect human health and the environment against the adverse effects resulting from the generation, management, transboundary movements and disposal of hazardous and other wastes.
- Montreal Protocol The Montreal Protocol was a globally coordinated regulatory action that sought to regulate ozone-depleting chemicals. 191 countries have ratified the treaty.

Rotterdam Convention –

- The text of the Convention was adopted on 10 September 1998 by a Conference in Rotterdam, the Netherlands. The Convention entered into force on 24 February 2004. The Convention creates legally binding obligations for the implementation of the Prior Informed Consent (PIC) procedure.
- to promote shared responsibility and cooperative efforts among Parties in the international trade of certain hazardous chemicals in order to protect human health and the environment from potential harm
- to contribute to the environmentally sound use of those hazardous chemicals, by facilitating information exchange about their characteristics, by providing for a national decision-making process on their import and export and by disseminating these decisions to Parties.

- Globally Harmonized System of Classification and Labeling of Chemicals (GHS)
 - Proposes harmonized hazard communication elements, including labels and safety data sheets.
 - It was adopted by the United Nations Economic Commission for Europe (UNECE) in 2002.
 - This system aims to ensure a better protection of human health and the environment during the handling of chemicals, including their transport and use.
 - The classification of chemicals is done based on their hazard.

Chemical Labels



- Strategic Approach to International Chemicals Management (SAICM) –
 - Adopted at the International Conference on Chemicals Management (ICCM), which took place from 4–6 February 2006 in Dubai, gathering governments and intergovernmental and non-governmental organizations.
 - It defines a policy framework to foster the sound worldwide management of chemicals.
 - Covers risk assessments of chemicals
 - Harmonized labeling
 - SAICM is a voluntary agreement.

Useful Websites

- EPA's TRI home page: <u>www.epa.gov/tri</u>
- Emergency Planning & Community Right-to-Know Act (EPCRA): <u>http://www.epa.gov/lawsregs/laws/epcra.html</u>
- EPA Compliance and Enforcement: <u>http://www.epa.gov/compliance/</u> [access to information on EPA' s civil and criminal enforcement activities]
- Scorecard, The Pollution information site <u>http://scorecard.goodguide.com/</u>

Some Useful Websites

- National Library of Medicine toxics page: <u>www.toxnet.nlm.nih.gov</u> [Another searchable entry point for TRI data]
- Edison Electric Institute's TRI page: <u>http://www.eei.org/ourissues/TheEnvironment/Air/Pages/</u> <u>ToxicsRelInv.aspx</u>

[A good example of an industry perspective. The page contains industry policy positions, public-relations material, and information for electric utilities on how to comply with TRI reporting requirements.]

AIR POLLUTION

AIR POLLUTION WORLDWIDE

The Bad News

- 3 million people worldwide die each year as a result of air pollution (WHO estimate)
- 2 million of these die from indoor air pollution (WHO estimate)
- Delhi air pollution causes 10,000 premature deaths/y
- 1.5 years of lost life expectancy in U.S. and EU cities with dirtiest air (Lancet study)

AIR POLLUTION WORLDWIDE

The Good News

- Substantial improvements in the last 20 years in many countries.
- Lead banned in fuels in many countries

Air Pollution Sources

- Stationary = fixed sources of emissions → e.g. power plants, refineries, gas stations
- Area = emissions uniformly distributed in an area → road dust, open burning, lawn mowing, consumer products, pesticide spraying
- Mobile = sources move around → cars, trucks, boats, airplanes

Sources Refineries Manufacturing Food processing **Electric utilities** Chemical production

Stationary



Area-Wide Sources Farming Paved & unpaved road dust Solvents Consumer products Open burning



WHAT IS PARTICULATE MATTER?



Complex Mixture
WHERE DO PARTICLES COME FROM?



HOW SMALL IS PM?



PM10 AND PM2.5 SIZE VS. COMPOSITION



Particles in the Respiratory Tract



Fine particulates are deposited much more deeply in the respiratory tract than coarse particulates

Figure 13–1 Aerodynamic deposition of particles by size in the respiratory tract (nasopharyngeal: nose and throat regions; tracfieobronchial: tubes leading to lungs; pulmonary: lung regions). Source: Air Quality Criteria for Particulate Matter, National Air Pollution Control Administration, Publication AP 49, 1960

Diesel Fuel

- Particulate matter (diesel engines emit 60% of particulates that comes from vehicles)
- Diesel fuel contains many volatile organic compounds known to be toxic: benzene, formaldehyde, 1,3-butadiene, and polycyclic aromatic hydrocarbons
- More than 40 hazardous air pollutants (HAPs) are in diesel exhaust.
- Associated with multiple health risks: asthma, cancer, genetic damage

Diesel Emissions Reduction



Important Concepts

- Environmental concentration = mass of pollutant per unit volume or mass of air, water, food, soil, etc.
- Exposure = concentration in medium × duration of contact
- Intake = mass of substance taken into body = concentration × volume of intake
- Retained dose = mass of substance retained in body after intake and initial excretion
- Body burden = stock of substance in the body at a given time (also, organ burden, bone burden)
- Dose-response relation = probability of adverse health impact as a function of exposure or dose
- Standard = maximum acceptable emission level or environmental concentration permitted by regulation

Environmental Concentration Units

Gaseous air pollutants: ppmv, ppbv, pptv, mg/m³, µg/m³, ng/m³ Particulate air pollutants: mg/m^3 , $\mu g/m^3$, ng/m^3 Water pollutants: mg/L, μ g/L, ng/L Pollutants in food, soils: mg/kg Example: Convert primary SO₂ standard from ppmv to μ g/m³ SO₂ std (in ppmv) = 0.03 ppmv @ 25 °C

$$\frac{\mu g SO_2}{m^3} = \frac{0.03 \text{ mol SO}_2}{1 \text{ million mol air}} \left(\frac{1 \text{ million mol air}}{10^6 \text{ mol air}}\right) \left(\frac{64.065 \text{ g SO}_2}{1 \text{ mol SO}_2}\right) \left(\frac{10^6 \mu g}{1 \text{ g}}\right) \left(\frac{1 \text{ mol air}}{24.8 \text{ Lair}}\right) \left(\frac{10^3 \text{ L}}{1 \text{ m}^3}\right)$$
$$= 77 \ \mu g SO_2/m^3$$

Exposure & Intake

3 main routes of exposure and intake

- oral
- inhalation
- dermal (skin)

2 main types of exposure

- Acute short duration, high intensity
- Chronic long duration, lower intensity

Timing of exposure

- Continuous vs. intermittent
- Number of exposures
- Duration each time exposed

Calculating Intake

Example: If you inhale 20 m³ of air a day that contains the standard for SO₂, calculate your daily inhalation intake of SO₂ in mg SO₂/day.

$$\frac{\text{mg SO}_2}{\text{day}} = \frac{77 \,\mu\text{g SO}_2}{1 \,\text{m}^3} \left(\frac{20 \,\text{m}^3}{1 \,\text{day}}\right) \left(\frac{1 \,\text{g}}{10^6 \,\mu\text{g}}\right) \left(\frac{10^3 \,\text{mg}}{1 \,\text{g}}\right) = 1.5 \,\text{mg SO}_2/\text{day}$$



Figure 3-1. Routes of absorption, distribution, and excretion of toxicants in the body.

Health Effects: Dose Response

"What is it that is not poison? All things are poison and nothing is without poison. It is the dose only that makes a thing a poison." -- Paracelsus, 16th century





Health Effects: Dose Response

- Two main methods of determining the health effects (response) of toxic exposure
 - toxicology → experimental laboratory testing, often with animals → known doses and body burdens
 - epidemiology \rightarrow statistical analysis of medical or public health data \rightarrow environmental exposures
- Ethics is often an obstacle to better understanding of health effects through human and animal testing
- Where we have direct evidence for effects on humans it often comes from occupational or accidental exposures coal miners, Hiroshima survivors, etc.

Acute Toxicity

Acute toxicity = adverse health effects of short term exposure Acute Toxicity Measures

- LD-50 = dose at which 50% of exposed population will die
- LC-50 = the concentration of the chemical in air that kills 50% of the test animals in a given time (usually four hours) is the LC_{50} value.

Example:

Oral LD-50 for parathion = 3 mg/kg (i.e. 3 mg of parathion per kg of body weight). What is 50% lethal dose for: Adult weighing 70 kg: 70 kg × 3 mg/kg = 210 mg Toddler weighing 10 kg: 10 kg × 3 mg/kg = 30 mg

Substance	Animal, Route	LD ₅₀ {LC ₅₀ }
Water	rat, oral	90,000 mg/kg
Vitamin C (ascorbic acid)	rat, oral	11,900 mg/kg
Grain alcohol (ethanol)	rat, oral	7,060 mg/kg
Table Salt	rat, oral	3,000 mg/kg
Aspirin (acetylsalicylic acid)	rat, oral	200 mg/kg
Caffeine	rat, oral	192 mg/kg
Nicotine	rat, oral mice, oral	50 mg/kg 3.3 mg/kg
Sodium cyanide	rat, oral	6.4 mg/kg
Ricin	rat, intraperitoneal rat, oral	22 µg/kg 20-30 mg/kg
Dioxin (TCDD)	rat, oral	20 µg/kg
VX (nerve agent)	human, oral, inhalation, absorption through skin/eyes	2.3 µg/kg (estimated)
Polonium-210	human, inhalation	10 ng/kg (estimated)
Botulinum toxin	human, oral, injection, inhalation	1 ng/kg (estimated)
Ionizing radiation	human, irradiation	3-6 <u>Gy</u>

Chronic Toxicity "Endpoints"

Somatic effects (effects on the body)

- <u>Carcinogenesis</u>: uncontrolled cell division leading to cancer
- <u>Neurotoxicity</u>: cognitive, sensory, and motor impairments
- <u>Immunotoxicity</u>: suppressed or exaggerated immune function
- <u>Toxic syndromes of organs</u>: respiratory, cardiovascular hepatic (liver) disease or malfunction, etc.
- Reproductive damage
- <u>Mutagenesis</u>: faulty DNA replication
- <u>Teratogenesis</u>: Developmental toxicity harm to a fetus

Different Shapes of Dose-Response Curve



Describing Toxic Risk: Carcinogens

Slope factor = the slope of the line expressing how much cancer risk increases per milligram of the substance ingested/inhaled per kilogram of body weight per day

Unit risk = the cancer risk resulting from a continuous exposure to a "unit" concentration of a carcinogen (e.g. continuous exposure to 1 mg/L or 1μ g/m³)

Acceptable concentration = concentration of a carcinogen in water or air that results in an "acceptable" risk (often 10^{-6}) for a continuous (usually lifetime) exposure to that concentration

Example: Benzo(a)pyrene (BAP)



- BAP oral slope factor 11.5 cancer/mg/kg·day = $\frac{11.5 \text{ cancer}}{1 \text{ mg/kg·day}} = \frac{11.5 \text{ cancer·kg·day}}{1 \text{ mg}}$
- Convert to unit risk: divide by mass of subject (e.g. 70 kg) and multiply by daily consumption (e.g. 2 liters of H₂O per day):

$$\frac{2 \operatorname{cancer}}{\operatorname{mg/L}} = \frac{2 \operatorname{L-cancer}}{\operatorname{mg}} = \frac{11.5 \operatorname{cancer} \cdot \operatorname{kg} \cdot \operatorname{day}}{1 \operatorname{mg}} \left(\frac{2 \operatorname{L}}{1 \operatorname{day}}\right) \left(\frac{1}{70 \operatorname{kg}}\right) = 0.3 \operatorname{cancer/mg/L}$$



• To find the BAP concentration that gives a 1 in a million cancer risk, divide 10⁻⁶ by the unit risk:

$$\frac{? \text{ ng/L}}{\text{million cancers}} = \frac{? \text{ ng}}{\text{million cancers} \cdot L}$$
$$= \frac{\text{mg}}{0.3 \text{ cancer} \cdot L} \left(\frac{1 \text{ cancer}}{10^6 \text{ cancers}}\right) \left(\frac{1 \text{ g}}{10^3 \text{ mg}}\right) \left(\frac{10^9 \text{ ng}}{1 \text{ g}}\right)$$
$$= 3 \text{ ng/L}$$

Describing Toxic Risk: Non-Carcinogens

- NOAEL = no observable adverse effects level = the dose at which there is no observed adverse effect → de facto threshold
- RfD = reference dose = the daily oral dose that poses no likely health risk over a lifetime

Air Pollution Regulation in the U.S.

 The Clean Air Act, which was enacted in 1970 and last amended in 1990, requires EPA to set National Ambient Air Quality Standards for pollutants considered harmful to public health and the environment.

http://www.epa.gov/air/caa/

http://www.epa.gov/air/criteria.html

- US EPA sets federal air quality standards which provides legal basis for regulation
- Emissions are regulated by state agencies to comply with federal standards

Clean Air Act Classifications

 7 Criteria Air Pollutants: SO_X, NO_X, CO, Pb, PM₁₀, PM_{2.5}, O₃ Health-based standards for ambient concentrations

http://www.epa.gov/air/urbanair/

188 Hazardous Air Pollutants (HAPs)
e.g. benzene, chromium, formaldehyde
Best-available technology standards

Ambient Air Quality Standards

· · · · · · · · · · · · · · · · · · ·							
Pollutant Averagin		g California Standards 1		Federal Standards ²			
	Time	Concentration ³	Method ⁴	Primary 3,5	Secondary 3,8	'Method 7	
Ozone (O ₃)	1 Hour	0.09 ppm (180 µg/m³)	Ultraviolet Photometry	0.12 ppm (235 μg/m ³) ⁸	Same as Primary Standard	Ethylene Chemiluminescence	
	8 Hour	—		0.08 ppm (157 μg/m ³)			
Respirable Particulate	Annual Geometric Mean	30 µg/m²	Size Selective Inlet Sampler	_	Same as	Inertial Separation and	
Matter	24 Hour	50 µg/m²	ARB Method	150 µg/m ³	Primary Standard	Gravimetic	
(PM ₁₀)	Annual Arithmetic Mean	-	P (8/22/85)	50 µg/m³		Analysis	
Fine Particulate	24 Hour	No Separate State Standard		65 µg/m³	Same as Si	Inertial Separation and	
Matter (PM ₂₅)	Annual Arithmetric Mean			15 μg/m ^b	Primary Standard	Ĝravimetic Analysis	
Carbon	8 Hour	9.0 ppm (10 mg/m ³)	Non-dispersive Infrared Photometry	9 ppm (10 mg/m ³)	None	Non-dispersive Infrared Photometry (NDIR)	
Monoxide	1 Hour	20 ppm (23 mg/m ⁹)		35 ppm (40 mg/m ³)			
(CO)	8 Hour (Lake Tahoe)	6 ppm (7 mg/m ⁹)	(NDIR)	-			
Nitrogen Dioxide	Annual Arithmetric Mean	_	Gas Phase Chemiluminescence	0.053 ppm (100 µg/m³)	Same as Primary Standard	Gas Phase Chemiluminescence	
(NO ₃)	1 Hour	0.25 ppm (470 µg/m³)	Cathanna ann an a	-			
	30 days average	1.5 μg/m ³	AIHL Method 54	-	-	High Volume Sampler and Atomic Absorption	
Lead	Calendar Quarter	-	(12/74) Atomic Absorption	1.5 μg/m ³	Same as Primary Standard		
Sulfur Dioxide	Annual Arithmetric Mean	_		0.030 ppm (80 µg/m²)	-	Pararosoaniline	
	24 Hour	0.04 ppm (105 µg/m³)	Fluorescence	0.14 ppm (365 µg/m ³)	-		
(SO ₂)	3 Hour	-]	-	0.5 ppm (1300 µg/m³)		
	1 Hour	0.25 ppm (655 µg/m³)		-	-		

National Ambient Air Quality Standards

	Prima	ry Standards	Secondary Standards		
Pollutant	Level	Averaging Time	Level	Averaging Time	
<u>Carbon</u> Monoxide	9 ppm (10 mg/m ³)	8-hour ⁽¹⁾	None		
	35 ppm (40 mg/m ³)	1-hour ⁽¹⁾			
<u>Lead</u>	0.15 µg/m ^{3 <u>(2)</u>}	Rolling 3-Month Average	Same as Primary Same as Primary		
	1.5 µg/m ³	Quarterly Average			
<u>Nitrogen</u> Dioxide	53 ppb (3)	Annual (Arithmetic Average)	Same as Primary None		
	100 ppb	1-hour (4)			
Particulate Matter (PM ₁₀)	150 µg/m ³	24-hour (5)	Same as Primary		
Particulate Matter (PM _{2.5})	15.0 µg/m ³	Annual ⁽⁶⁾ (Arithmetic Average)	Same as Primary Same as Primary		
	35 µg/m ³	24-hour (7)			
<u>Ozone</u>	0.075 ppm (2008 std)	8-hour <u>(8)</u>	Same as Primary		
	0.08 ppm (1997 std)	8-hour ⁽⁹⁾	Same as Primary		
	0.12 ppm	1-hour (10)	Same as Primary		
<u>Sulfur</u> Dioxide	0.03 ppm	Annual (Arithmetic Average)	0.5 ppm	3-hour (1)	
	0.14 ppm	24-hour (1)			
	75 ppb (11)	1-hour	None		

Air Pollution in U.S. – Current

Changes since 1970:

- Pb removal from gasoline a great triumph
- CO, NO_X, SO₂ greatly reduced
- Ozone greatly reduced but still a problem in some areas
- PM, diesel, HAP, greatest current air pollution health concerns

Research trends and questions:

- Increasing reliance on epidemiology over toxicology
- Need for finer resolution in exposure studies
- Increasing evidence that cardiovascular impacts
- Synergistic effects among pollutants
- Pollution transport across air basins
- Understanding what causes health effects of PM

Reducing Power Plant Emissions

- SO₂ emissions
 - fuel switching \rightarrow coal to natural gas (0.001% S)
 - fuel switching \rightarrow high-sulfur coal to low-sulfur coal
 - sulfur removal (solvent refining can remove up to 75% S)
 - flue-gas desulfurization (FGD) -- smokestack "scrubbers"
 - add lime to exhaust gas: CaO + SO₂ + 1/2 O₂→ CaSO₄ (gypsum)
- NO_X emissions
 - modify combustion process: fuel mix, temperature
 - SCR selective catalytic reduction (removes up to 75% NO_x)
- Particulates
 - fabric filters "baghouse"
 - ESP electrostatic precipitators
 - removes > 90% of particulate matter

Wet SO₂ Scrubber



Using limestone: Using lime: $\begin{aligned} &\mathsf{CaCO}_3 \ (\mathsf{solid}) + \mathsf{SO}_2 \ (\mathsf{gas}) \to \mathsf{CaSO}_3 \ (\mathsf{solid}) + \mathsf{CO}_2 \ (\mathsf{gas}) \\ &\mathsf{Ca(OH)}_2 \ (\mathsf{solid}) + \mathsf{SO}_2 \ (\mathsf{gas}) \to \mathsf{CaSO}_3 \ (\mathsf{solid}) + \mathsf{H}_2\mathsf{O} \ (\mathsf{liquid}) \end{aligned}$

Electrostic Precipitator (ESP)







Selective Catalytic Reduction



 $4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O$ $2NO_2 + 4NH_3 + O_2 \rightarrow 3N_2 + 6H_2O$ $NO + NO_2 + 2NH_3 \rightarrow 2N_2 + 3H_2O$

Reducing Vehicle Emissions: 3-Way Catalytic Converters



Clean Fuel / Clean Technology Options	Type of Engine	Percent Reduction in Emissions of Particulate Matter	Percent Reduction in Emissions of Nitrogen Oxides	Approximate Cost of Technology
Ultra-Low Sulfur Diesel (ULSD)	Nonroad Diesel Engine	About 5 to 9% Enables the PM filter technology to work	N/A	8 to 20 cents per gallon more than regular diesel now
Particulate Matter Filter	New or Used Diesel Engine - 1995 or newer models	60 to 90%	N/A	\$5,000 to \$10,000 Must use ULSD fuel
Oxidation Catalyst	New or Used Diesel Engine	20 to 30%	N/A	\$1,000 to \$2,000 and can be used with regular diesel
Compressed Natural Gas (with an oxidation catalyst)	New CNG Engines	70 to 90% if using catalyst technology to reduce ultra fine PM, formaldehyde, and methane - otherwise, methane and aldehydes will be much higher than diesel engines	About 60% reduction but are highly variable (sometimes increases occur)	\$30,000 more than a diesel bus (cost of CNG fuel similar to regular diesel fuel) Very expensive special re- fueling infrastructure and maintenance facilities are required
Biodiesel Fuel B20: 20% biodiesel, 80% regular diesel B100: 100% biodiesel	New or Used Diesel Engine	B20 - 10% B100 - 40%	Biodiesel increases emissions of NOx slightly. B20 blend +2% B100 fuel +10%	B20 - 5 to 30 cents per gallon more than regular diesel B100 - 75 cents to \$1.50 per gallon more than regular diesel (B100 may not be an option in the winter season)
Emulsified Diesel Fuel	New or Used Diesel Engine	About 50%	About 10%	20 cents per gallon more than regular diesel fuel

Percent Change in Air Quality

	1980 vs 2010	1990 vs 2010	2000 vs 2010
Carbon monoxide (CO)	-82	-73	-54
Ozone (O_3) (8-hr)	-28	-17	-11
Lead (Pb)	-90	-83	-62
Nitrogen dioxide (NO ₂) (annual)	-52	-45	-38
PM ₁₀ (24-hr)		-38	-29
PM _{2.5} (annual)			-27
PM _{2.5} (24-hr)			-29
Sulfur Dioxide (SO ₂) (24-hr)	-76	-68	-48

Comparison of Growth Measures and Emissions, 1999-2010



http://www.epa.gov/airtrends/2011/report/airpollution.pdf