# Module 4:

# Pollutant Types and Emission Sources

## Significant Pollutants of Interest

- Key air pollutants for which ambient air quality standards are being established by some countries:
  - Carbon monoxide (CO)
  - Nitrogen oxides ($NO_x$)
  - Sulfur dioxide ($SO_2$)
  - Lead (Pb)
  - Particulate matter (PM)
  - Dustfall
  - "Air Toxics" such as Benzene**
  - Ozone ($O_3$)
  - Mercury (Hg)

**You can find more information on the U.S. EPA's air toxics program at www.epa.gov/ttn/atw/, and the list of 188 at http://www.epa.gov/ttn/atw/188polls.html

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# Emissions Inventory Sources

- Point (individual plants)
- Non-Point
  - Stationary Area
- Onroad & Nonroad Mobile
- Natural Sources

For overview of the U.S. EPA's air programs, go to
http://www.epa.gov/oar/oaqps/cleanair.html

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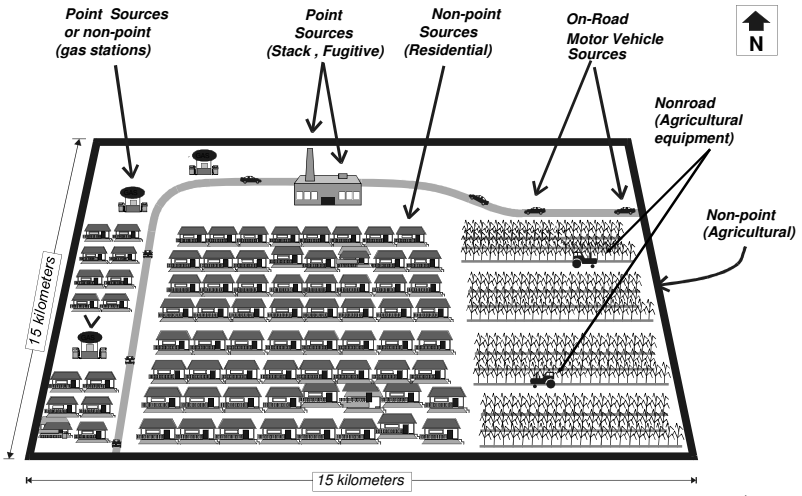
# Emission Inventory Characteristics: Types of Emission Sources

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# U.S. EPA's "One-Atmosphere" Modeling and Management

- "One-Atmosphere" Approach :

  An integrated approach to address various air quality issues collectively under one modeling and management system.

- Why "One-Atmosphere" ?
  - Regulated sources perspective
  - Emitted pollutants perspective
  - Atmospheric chemistry perspective

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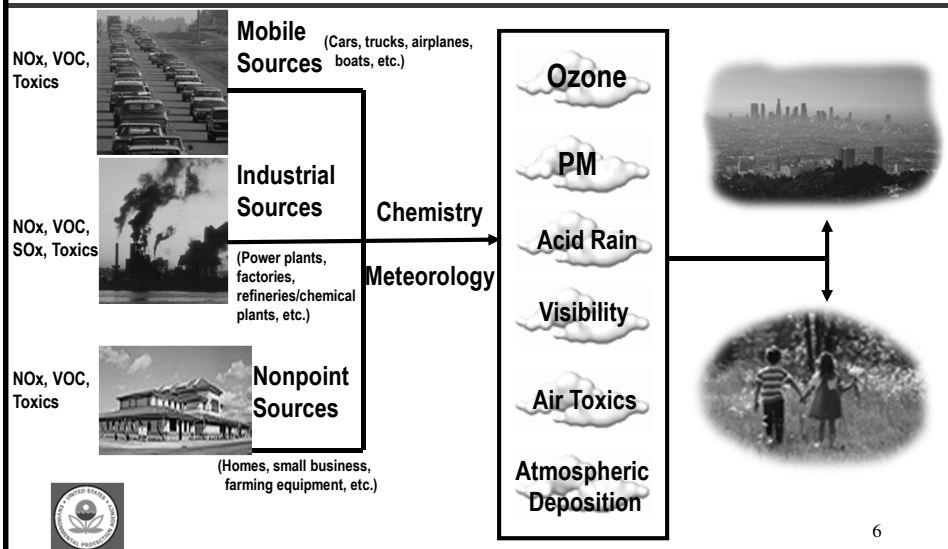
# Regulating Air Pollution : One-Atmosphere Approach

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## Pollutant Types and Emission Sources

- Training focuses on criteria pollutants:
  - For which air quality guidelines or standards have been or will be established
  - Emitted by point, nonpoint, on- and off-road mobile, and natural sources
  - Impacts on health and the environment
- Some pollutants are emitted directly (e.g., dust) and others are formed by chemical reaction (e.g., ozone from photochemical reactions)

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## Pollutant Types and Emission Sources (cont.)

- "One-Atmosphere" approach includes "air toxics" pollutants:
  - Which can be constituents of criteria pollutants or precursors such as VOC
  - Are also emitted by point, nonpoint, on- and non-road mobile, and natural sources
  - Also impacts health and the environment
- Like some criteria pollutants, some air toxics are emitted directly (e.g., benzene) and others are formed by chemical reaction (e.g., formaldehyde and acrolein from photochemical reactions)

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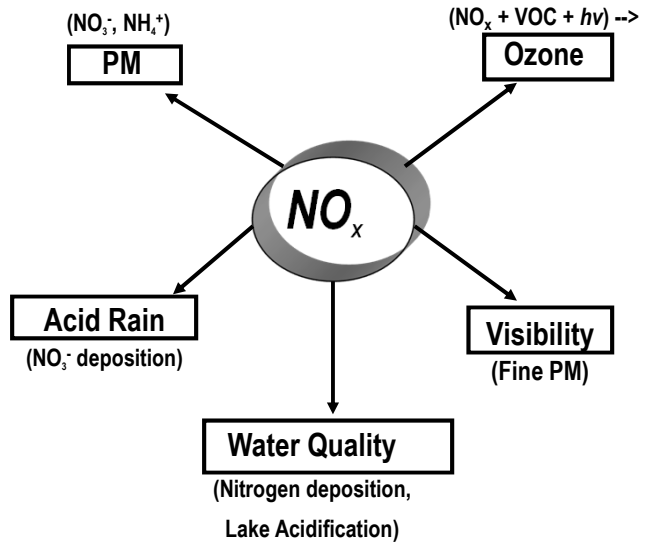
# $NO_x$-Related Air Quality Issues

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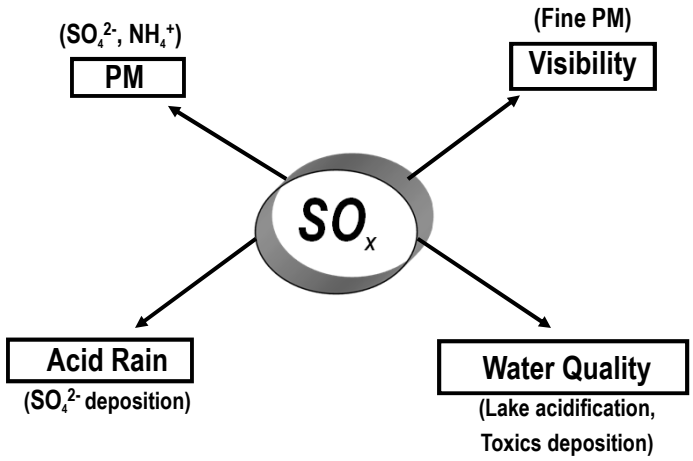
# $SO_x$-Related Air Quality Issues

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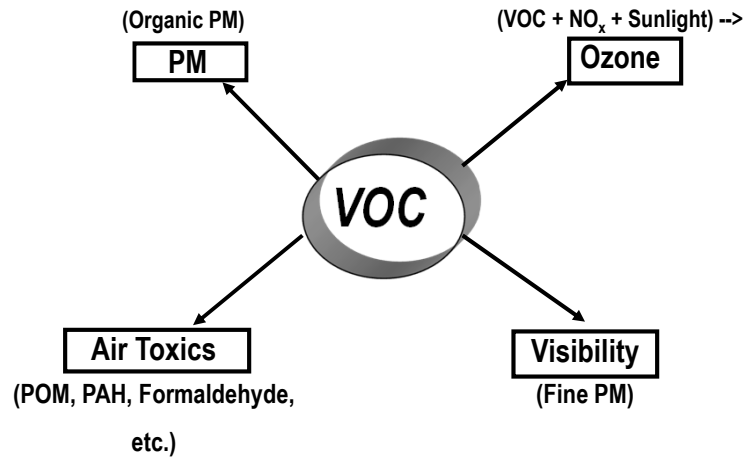
# VOC-Related Air Quality Issues

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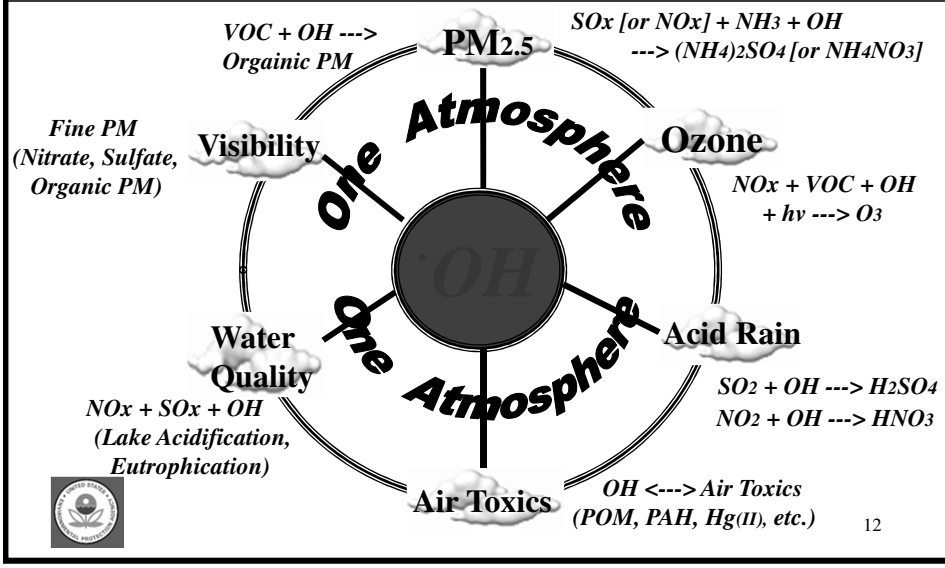
# ·OH Role in Pollutants Formation : One-Atmosphere

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# International Comparison of Air Quality Standards

| Pollutant | Duration of Exposure | WHO Guidelines | United States Standards | European Union Standards | China Standards Class I | Class II | Class III |
|---|---|---|---|---|---|---|---|
| CO (ppm) | 24-hour | | | | 3.49 | 3.49 | 5.24 |
| | 8-hour | 8.73 | 9[a] | 8.73 | | | |
| | 1-hour | 26.2 | 35[a] | | 8.73 | 8.73 | 17.47 |
| $NO_x$ (μg/m$^3$) | Annual | | 100 | 40 | 50 | 50 | 100 |
| | 24-hour | | | | 100 | 100 | 150 |
| | 1-hour | 200 | | 200[i] | 150 | 150 | 300 |
| Ozone (ppm) | 8-hour | 0.06 | 0.08[e] | 20 | | | |
| | 1-hour | | 0.12[f] | 50[h] | 0.06 | 0.08 | 0.10 |
| $PM_{10}$ (μg/m$^3$) | Annual | | 50[b] | 20 | 40 | 100 | 150 |
| | 24-hour | | 150[a] | 50[h] | 50 | 150 | 250 |
| $SO_2$ (μg/m$^3$) | Annual | 0.017 | 0.030 | | 0.007 | 0.021 | 0.035 |
| | 24-hour | 0.044 | 0.140[a] | 0.044[j] | 0.017 | 0.052 | 0.087 |

Footnotes

a) Not to be exceeded more than once per year
b) The expected annual arithmetic mean PM10 concentration at each monitor within an area must not exceed 15 μg/m$^3$.
e) The 3-year average of the 4$^{th}$-highest daily maximum 8-hr average ozone concentrations measured at each monitor within an area must be <=0.08 ppm.
f) The standard is attained when the expected number of days per calendar year with maximum hourly average concentrations above 0.12ppm is <=1.
g) Allowed <26 days of exceedances
h) Allowed <8 exceedances
i) Allowed <19 exceedances
j) Allowed <4 exceedances

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# Carbon Monoxide (CO)

- Created by incomplete combustion of carbonaceous fuel
- Sources
  - Automobiles
  - Residential heating and cooking
  - Industrial processes
  - Open burning
  - Prescribed or agricultural burning

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# Effects of Carbon Monoxide

- Global warming potential
- Health effects
  - Heart diseases
  - Prohibits the oxygen carrying ability of blood
  - Respiratory problems
  - Affects the central nervous system
  - Death at higher concentrations

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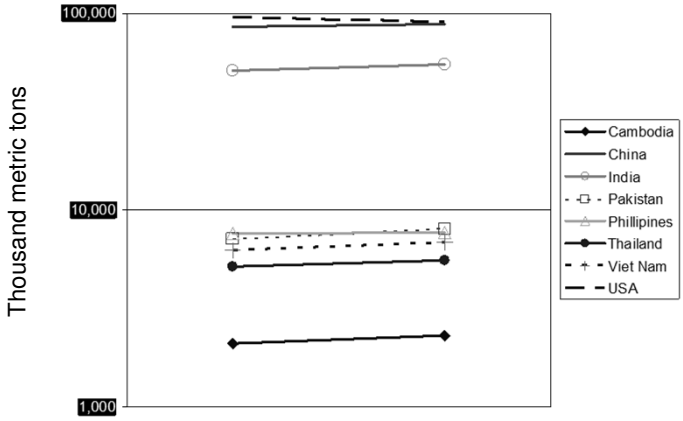
# CO Emission Trends (1990 to 1995)




Source: http://earthtrends.wri.org

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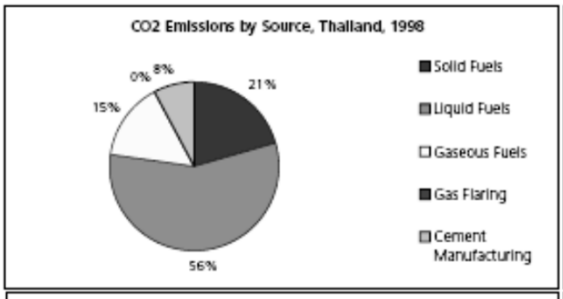
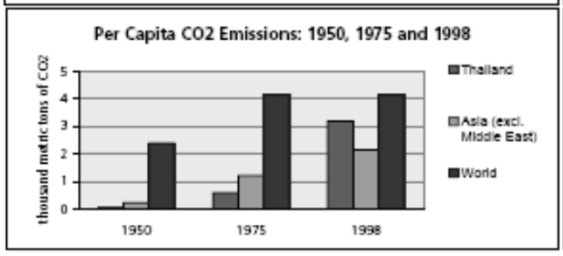
# $CO_2$ Emissions in Thailand




Source:
http://earthtrends.wri.org

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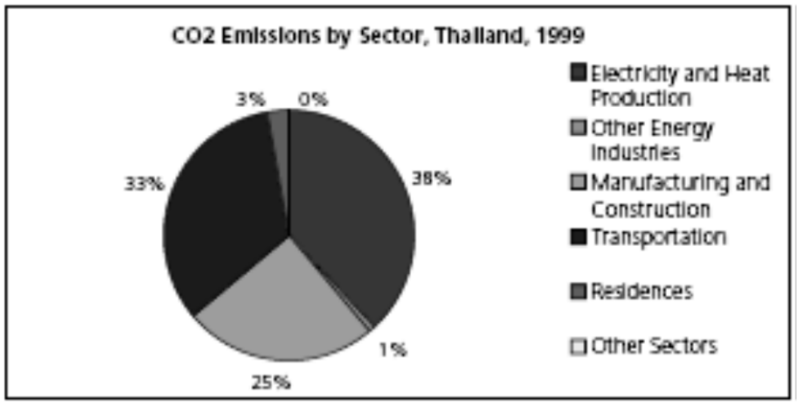
# $CO_2$ Emissions in Thailand (cont.)




Source: http://earthtrends.wri.org

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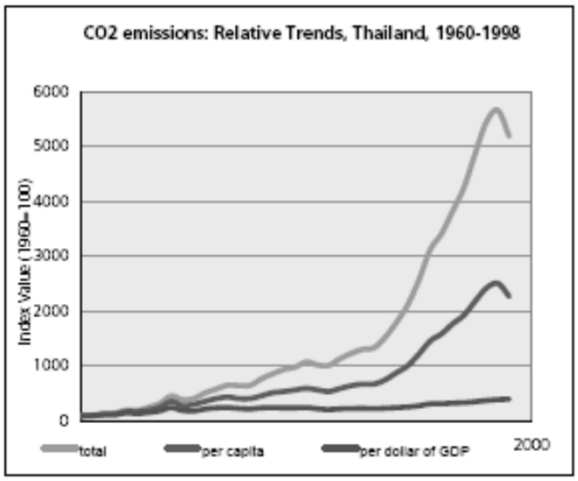
# $CO_2$ Emissions in Thailand (cont.)




Source: http://earthtrends.wri.org

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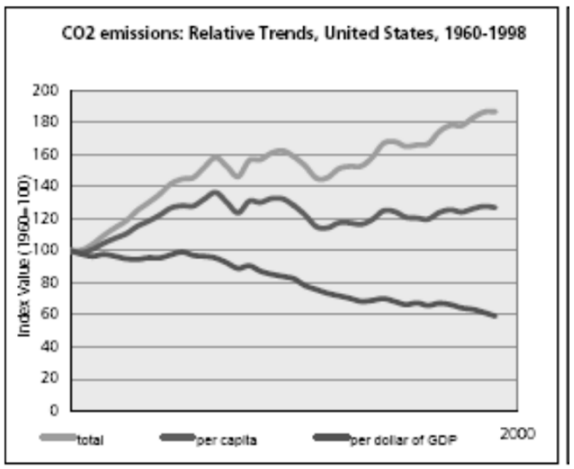
# $CO_2$ Emissions in the United States




Source: http://earthtrends.wri.org

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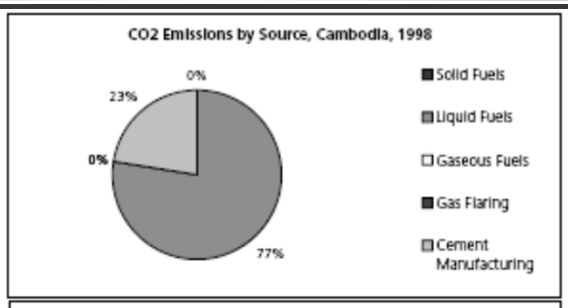
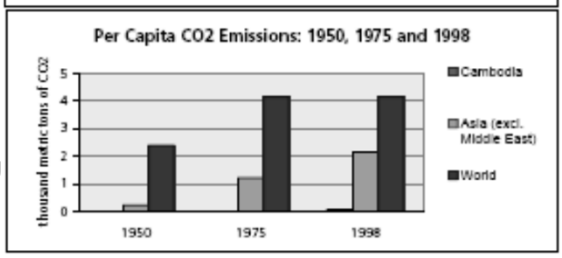
# $CO_2$ Emissions in Cambodia




Source:
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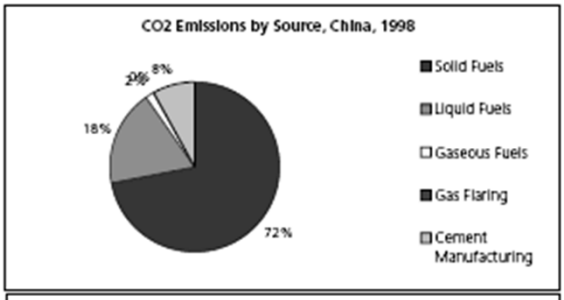
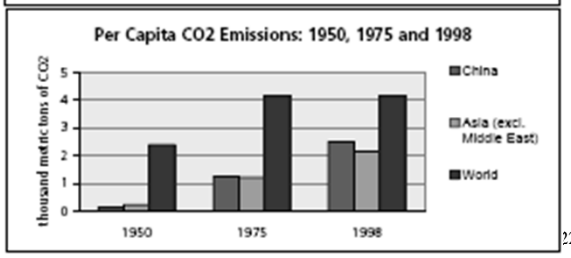
# $CO_2$ Emissions in China

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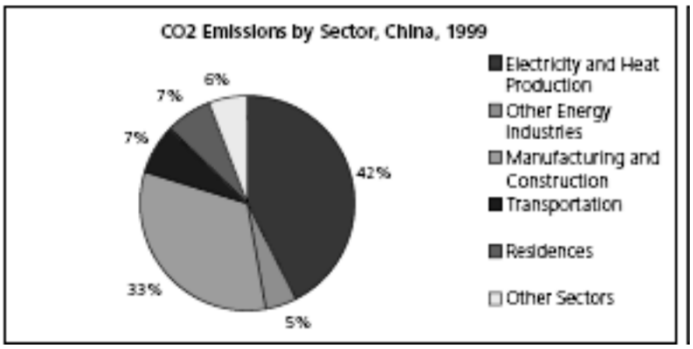
# $CO_2$ Emissions in China (cont.)

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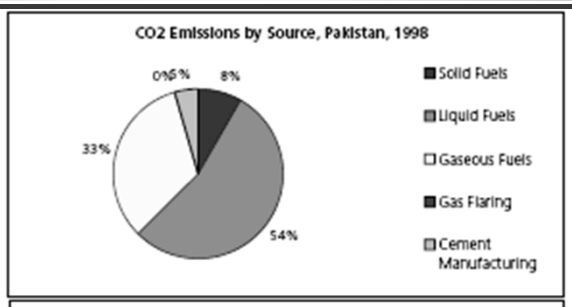
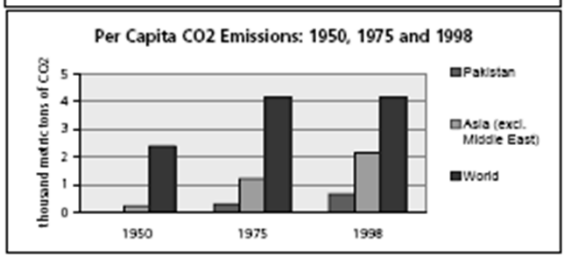
# $CO_2$ Emissions in Pakistan

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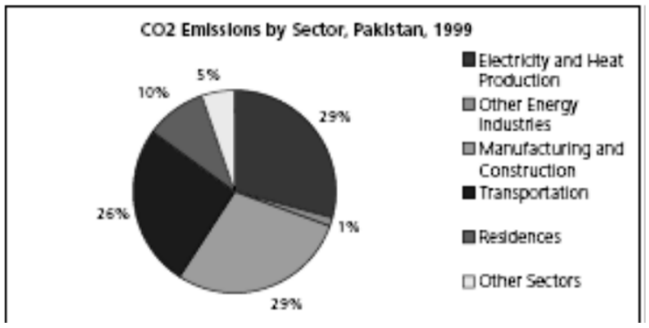
# $CO_2$ Emissions in Pakistan (cont.)

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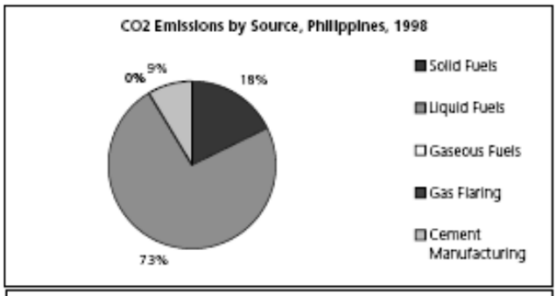
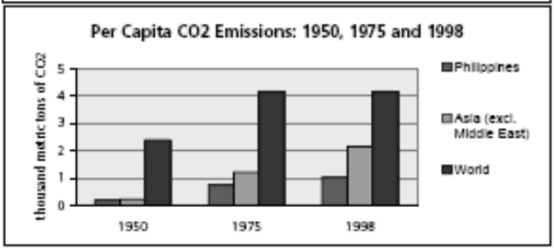
# $CO_2$ Emissions in Phillipines




Source:
http://earthtrends.wri.org

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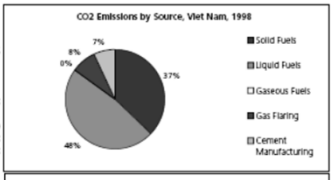
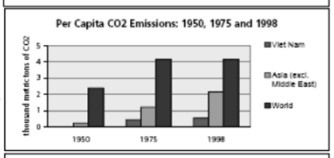
# $CO_2$ Emissions in Viet Nam

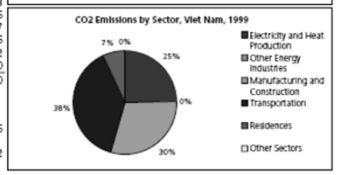
**Climate and Atmosphere-- Viet Nam**

EarthTrends Country Profiles

| Carbon Dioxide (CO2) Emissions (a) (in thousand metric tons of CO2) | Viet Nam | Asia (excl. Middle East) | World |
|---|---|---|---|
| Total Emissions, 1998 | 43,864 | 7,360,942 | 24,215,376 |
| Percent change since 1990 | 95% | 38% | 8% |
| Emissions as a percent of global CO2 production | 0.2% | 30.4% | |
| Emissions in 1998 from: | | | |
| solid fuels | 16,349 | 4,020,885 | 8,654,368 |
| liquid fuels | 20,951 | 2,304,231 | 10,160,272 |
| gaseous fuels | 26 | 580,898 | 4,470,080 |
| gas flaring | 3,549 | 22,391 | 172,208 |
| cement manufacturing | 2,990 | 432,537 | 758,448 |
| Per capita CO2 emissions, 1998 (thousand metric tons of CO2) | 0.5 | 2.1 | 4.1 |
| Percent change since 1990 | 69% | 19% | -2% |
| CO2 emissions (in metric tons) per million dollars Gross Domestic Product (b), 1998 | 1,732 | X | 773 |
| Percent change since 1990 | 5% | X | -10% |
| Cumulative CO2 emissions, 1900-1999 (in billion metric tons) | 969 | 161,972 | 933,686 |
| **CO2 Emissions by Sector, 1999 (c) (in million metric tons of CO2)** | | | |
| Public electricity, heat production, and autoproducers | 8 | 2,697 | 8,693 |
| Other Energy Industries | 0 | 312 | 1,205 |
| Manufacturing Industries and Construction | 10 | 1,915 | 4,337 |
| Transportation | 13 | 943 | 5,505 |
| Residential | 2 | 471 | 1,802 |
| Other Sectors (d) | X | 580 | 5,640 |
| Total Emissions All Sectors: | X | 6,918 | 27,180 |
| **CO2 Intensity, 1999** | | | |
| Emissions per total energy consumption (metric tons CO2 per terajoule energy) | 25 | 56 | 56 |
| Emissions per Gross Domestic Product (e) (metric tons of CO2/million $PPP) | 259 | 540 | 582 |




View more Country Profiles on-line at http://earthtrends.wri.org

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# Nitrogen Oxides ($NO_x$)

- $NO_x$ includes two primary species
  - Nitric oxide (NO)
  - Nitrogen dioxide ($NO_2$)
- Formed when fuel is burned
  - Nitrogen and oxygen in air => $NO_x$
  - Organically bound nitrogen in fuels form $NO_x$
- $NO_x$ is highly reactive and a major ozone precursor

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## $NO_x$ Sources in Southeast Asia

- Vehicle traffic
- High-temperature combustion processes
  - Power plants (thermal and cogeneration)
  - Industrial combustion (fossil fuels)

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## Effects of Nitrogen Oxides

- Photochemical smog
- Ozone formation
- Visibility degradation
- Acid deposition
- Secondary particulate matter precursor
- Eutrophication
  - Nutrient buildup in water
- Human health effects
  - Respiratory problems
  - Lung diseases

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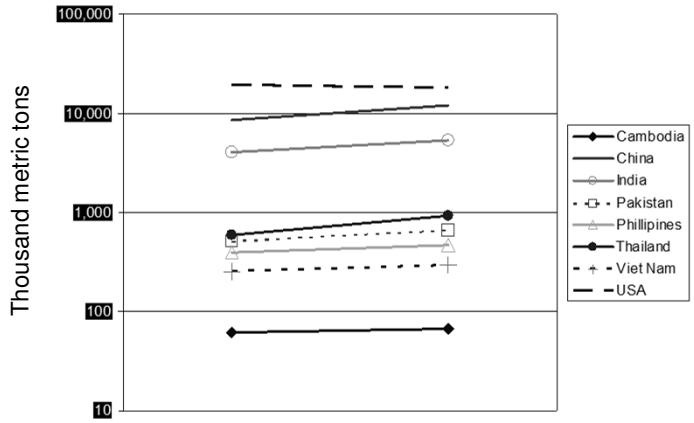
# $NO_x$ Emission Trends (1990 to 1995)




Source: http://earthtrends.wri.org

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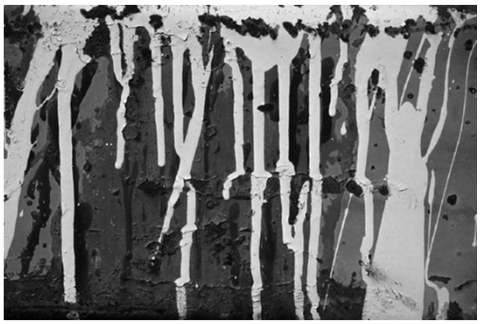
# Lead (Pb)

- A metal found naturally in the environment
- Used in manufactured products
- Sources of lead emissions in the air
  - Metal processing
  - Fuel combustion
  - Waste incinerators
  - Lead-acid battery manufacturing
  - Lead-based paint manufacturing



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## Effects of Lead

- Slowing of vegetative growth
- Elevated levels in water causing reproductive damage to some aquatic and animal life
- Health effects in humans
  - Damage to kidneys, liver, brain, and nerves
  - Leads to osteoporosis and reproductive disorders
  - Causes high blood pressure and increased risk of heart attacks

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## Particulate Matter (PM)

- Primary PM is directly emitted by dust and soot sources
- Secondary PM is formed by gas conversion reactions of $NO_x$, $SO_x$, VOCs, and $NH_3$
- PM size is an important property
  - Total suspended particulate (TSP) = 30 µm and larger
  - Respirable particulate = 10 µm and smaller ($PM_{10}$)
  - Fine particulate = 2.5 µm and smaller ($PM_{2.5}$)

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## Primary Particulate Matter Sources

- Industrial processes
- Industrial, commercial,
- residential fuel combustion
- Windblown dust (e.g., from mines)
- Reentrained dust from vehicle traffic on public and industrial roads
- Open burning, agricultural burning
- Natural sources (sea salt, volcanoes)

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## Effects of Particulate Matter

- Regional haze, visibility degradation
- Smog
- Soiling of buildings and property
- Alteration of local weather
- Health effects
  - Respiratory problems
  - Lung diseases
  - Premature death
  - Chronic bronchitis

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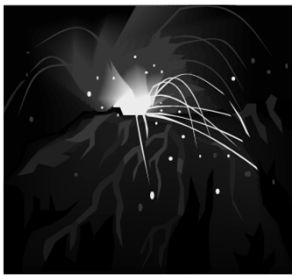
## Sulfur Dioxide ($SO_2$)

- Produced from combustion of sulfur-containing materials (e.g., coal)
- $SO_x$ used to categorize $SO_2$ and $SO_3$
- Sources
  - Fossil-fuel combustion
  - Industrial processes
  - Volcanoes



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## Effects of Sulfur Dioxide

- Visibility degradation
- Acid deposition
- Secondary particulate matter precursor
- Corrosion
- Human health effects
  - Respiratory problems
  - Lung diseases
  - Aggravation of existing cardio-vascular diseases

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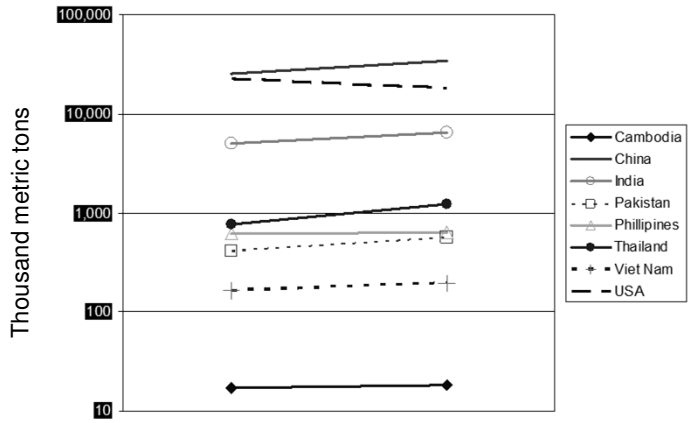
## SO2 Emission Trends (1990 to 1995)




Source: http://earthtrends.wri.org

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## Volatile Organic Compounds (VOCs)

- VOC species are part of the broad group of compounds called total organic gases (TOG)
- VOC species do not include organic compounds with limited or no photochemical reactivity
- VOCs are a significant contributor to ground-level ozone formation

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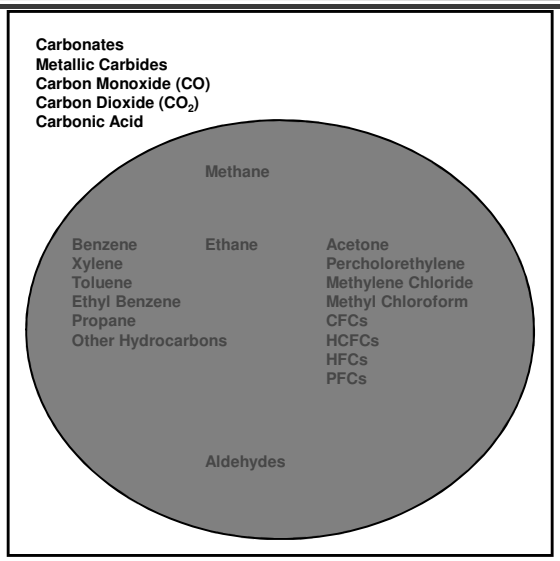
# Visual Representation of TOG/TOC Definition

Box includes all carbonaceous compounds

Shaded area includes total organic gases (TOG), also known as total organic compounds (TOC)

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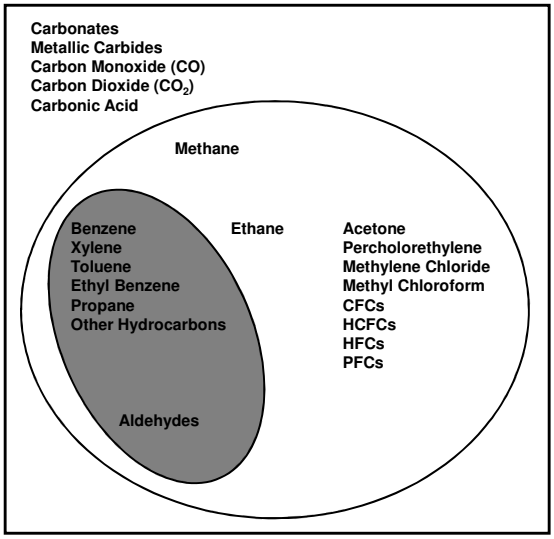
# Visual Representation of ROG/ROC/VOC Definition

Box includes all carbonaceous compounds

Shaded area includes reactive (or volatile) organic gases (ROG/ROC/VOC)

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## Common VOC Sources

- Combustion sources
  - Stationary fuel combustion
  - Vehicular traffic
- Evaporative sources
  - Surface coatings and paints
  - Petroleum product storage and distribution (e.g, at refineries, fuel stations)
  - Solvents (consumer products, industrial uses)

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## Effects of Volatile Organic Compounds

- Secondary aerosol formation (haze and particulate matter precursor)
- Photochemical smog, ground-level ozone formation
- Health effects
  - Respiratory problems
  - Nose and throat infections
  - Skin allergies
  - Cancer
  - Kidney, liver, and brain damage
  - Damage to nervous, reproductive and immune systems

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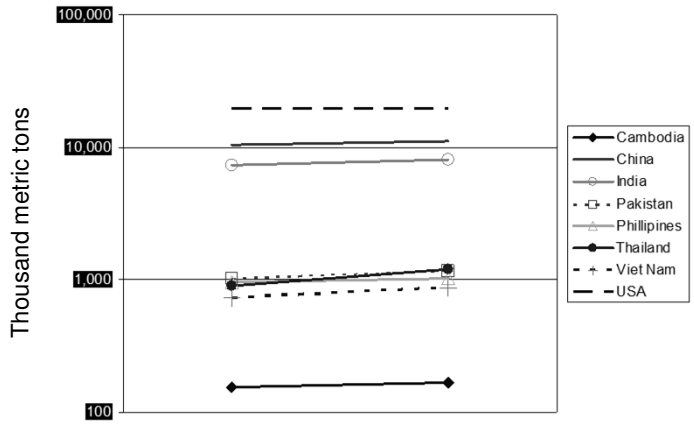
# VOC Emission Trends (1990 to 1995)




Source: http://earthtrends.wri.org

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# Mercury (Hg)

- Mercury is toxic, persistent, and bioaccumulates in food chains
- Mercury is released from various sources throughout the world
- These releases can be transported great distances through air and oceans, easily crossing national borders, cycling globally
- Even nations with minimal releases, and remote areas (such as the Arctic) are adversely affected
- Current releases add to the “global pool”…..

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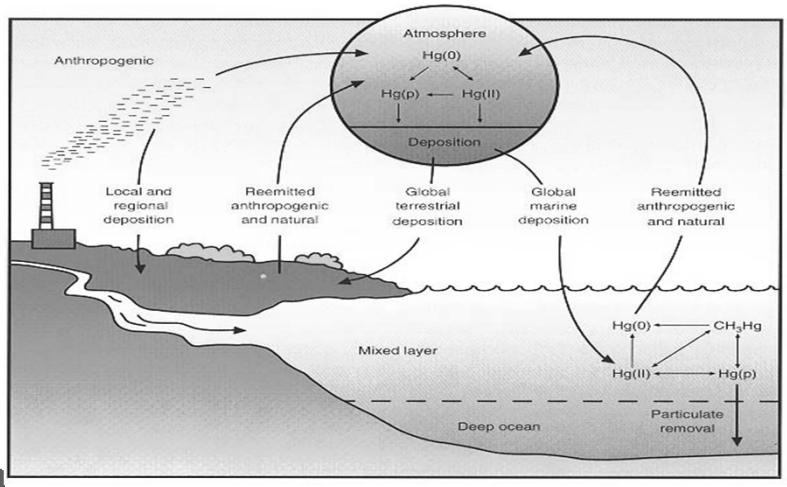
# Global Mercury Cycle




Courtesy of Rita Schoeny U.S. EPA. Adapted from U.S. Dept. of Interior's Report on Hg in the Florida Everglades

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# Globally, Many Humans/Wildlife May Be At Risk

- Generally due to consumption of significant amounts of contaminated fish;
- Also due to other sources of exposure (such as artisanal mining and other occupations, cosmetics, spills, ritualistic uses, etc…)

  - Note: Moderate consumption of a variety of fish is not likely to pose risks. Fish are a nutritious, beneficial food…..

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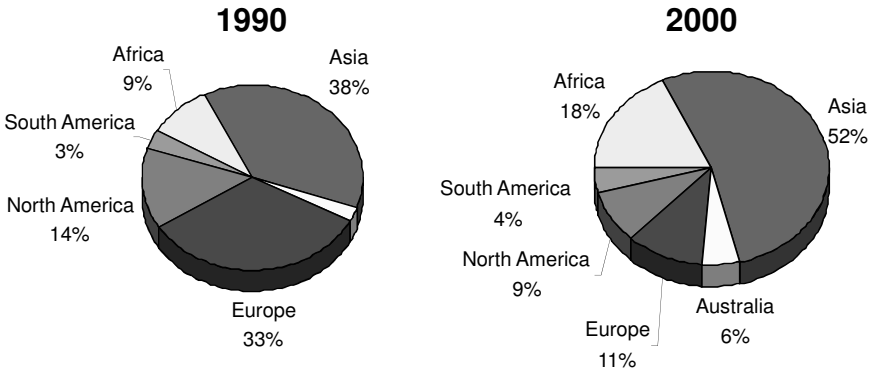
# Estimated Anthropogenic Emissions of Mercury by Region in 1990 and 2000




**Total: 1,881 metric tons/yr** **Total: 2,269 metric tons/yr**

Note: Significant emissions also occur due to natural sources, and re-emissions from historic anthropogenic sources.

Based on Pacyna, J., Munthe J., Presentation at Workshop on Mercury: Brussels, March 29-30, 2004

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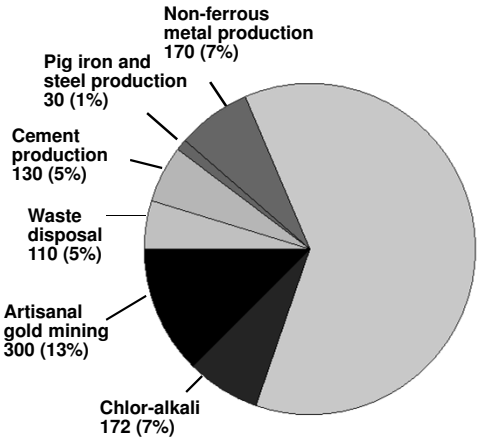
# Global Mercury Cycle




**Estimates are uncertain; most countries do not have Hg inventories**

**Total: 2,382 metric tons**

**Source: Estimates derived from data in the 2002 UNEP Global Mercury Assessment**

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## Examples of Hg Levels (ppm) in fish in Asia (values obtained from UNEP 2002, Table 4.5)

| Location | Fish Species | Hg Conc. |
|---|---|---|
| Australia | Redfin Perch | 0.12 – 1.3 |
| Fiji | Canned tuna | 0.01 – 0.97 |
| Hong Kong | Golden Thread | 0.22 |
| | Hair Tail | 0.146 |
| India | Fish, Bombay w. coast | 0.03 – 0.82 |
| Republic of Korea | 7 species, Kangkyung area, Keum River | Mean = 0.35 |
| Philippines | Tilapia | 0.1 – 0.5 |
| Thailand | 5 marine fish species | 0.05 – 0.7 |

**See UNEP Mercury Website: www.chem.unep.ch/mercury/** 51

## Major Exposure Pathways for Mercury

- Humans are exposed to 2 main mercury forms:
  Methylmercury (MeHg):
  - Primarily through ingestion of fish, and marine mammals (certain whales, seals) Elemental mercury ($Hg^0$) vapours:
  - Primarily from dental amalgams for most people
  - Occupations (such as artisanal mining and chloralkali plants) for some populations
  - Use of mercury in certain religious/cultural practices
  - Other incidents (children playing with mercury)
  - Spills (broken thermometers, thermostats, etc..)

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## Elemental ($Hg^0$) Mercury Vapor - Toxicity

- Inhalation main route of exposure
  - Readily crosses blood brain barrier and placenta
  - Nervous system is primary target of toxicity
  - Neurological effects include tremors, insomnia, memory loss, headaches
  - Also toxic to kidney
  - High exposures can cause death
  - In body, $Hg^0$ is oxidized to inorganic mercury ($Hg^{+2}$), which accumulates in kidney

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## What $Hg^0$ exposure levels are toxic? What levels are safe?

Long-term:

- Long-term occupational exposures to air levels of 25-30 ug/m$^3$ has resulted in adverse effects on nervous system + kidney
- U.S. EPA "reference concentration" = 0.1 ug/m$^3$ (safe exposure level for all humans over a lifetime)
- E.U. recommends that average annual exposure should not exceed 0.05 ug/m$^3$

Short-term:

- Short-term exposure to high concentrations can cause serious adverse effects
- Various Governments have established limits for worker exposures:
  For example, in India short-term (15 minutes) air levels can not exceed 30 ug/m$^3$

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## Exposures to Methylmercury (MEHg)

- Fish are an important/nutritious food, providing nutrients (protein, minerals/vitamins, etc…)
  - Ingestion of fish is also main source of exposure to MeHg
  - Levels of MeHg are generally much higher in fish (and marine mammals) compared to other foods
    - Typically about 0.05 to 1.4 ppm (or mg/kg) in fish
    - Levels vary by species, size, and age of fish
    - Also, vary by characteristics of waterbody (pH, redox potential, local contamination, and other factors)
    - Highest in large predatory marine species, such as shark, swordfish, large tuna, some whales
    - Levels can also be high in predatory freshwater fish, such as pike, perch, tilapia

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## Absorption and Metabolism

- >90% of Hg in fish is in the form MeHg
  - About 95% of ingested MeHg in fish is absorbed through the gastrointestinal tract
  - MeHg is distributed throughout the body and easily passes the placenta and blood brain barrier
  - Half-life in body has been measured to be 35 to 190 days (average = 72 days)

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## Methylmercury (MEHg) Toxicity

- MeHg is highly toxic, especially to developing nervous system
  - Also evidence of toxicity to cardiovascular, immune, and reproductive systems
  - Severe poisoning events occurred in 1960s-70s in Minamata Bay, Japan; and in Iraq:
    - Effects on adults included:
      - death, parathesia, tremors, ataxia, hearing and vision impairment, and balance and speech disturbances
    - Children born to mothers exposed during pregnancy exhibited:
      - cerebral palsy, delayed walking/talking, deficits in learning, and other effects

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## Preparing Emission Inventories for Modeling: "Emissions Processing"

- Typically, air quality models need detailed emission data inputs
- Work with modelers to understand what they need and ensure they know the limitations of the inventory
- Use emissions processing tools to prepare the inventory for use in air quality models

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## Preparing Emission Inventories for Modeling: "Emissions Processing" (cont.)

- Emission "Processors" are used to:
  - Spatially allocate the emissions from the inventory domain to a gridded modeling domain. Also, vertically allocate elevated point source emissions.
  - Temporally allocate annual emissions to hourly emissions
  - Speciate emissions into specific compound groups for photochemical modeling, or group/partition toxics
  - Project emissions to future year; with or without control strategies

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## Output from an Emissions Processor Is an Input to Air Quality Model

- Gridded emissions
- Speciated emissions
- Temporally allocated emissions
- Projected and controlled emissions
- Generally contains no specific information (plant names, descriptions)

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# Questions
# or
# Comments?

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