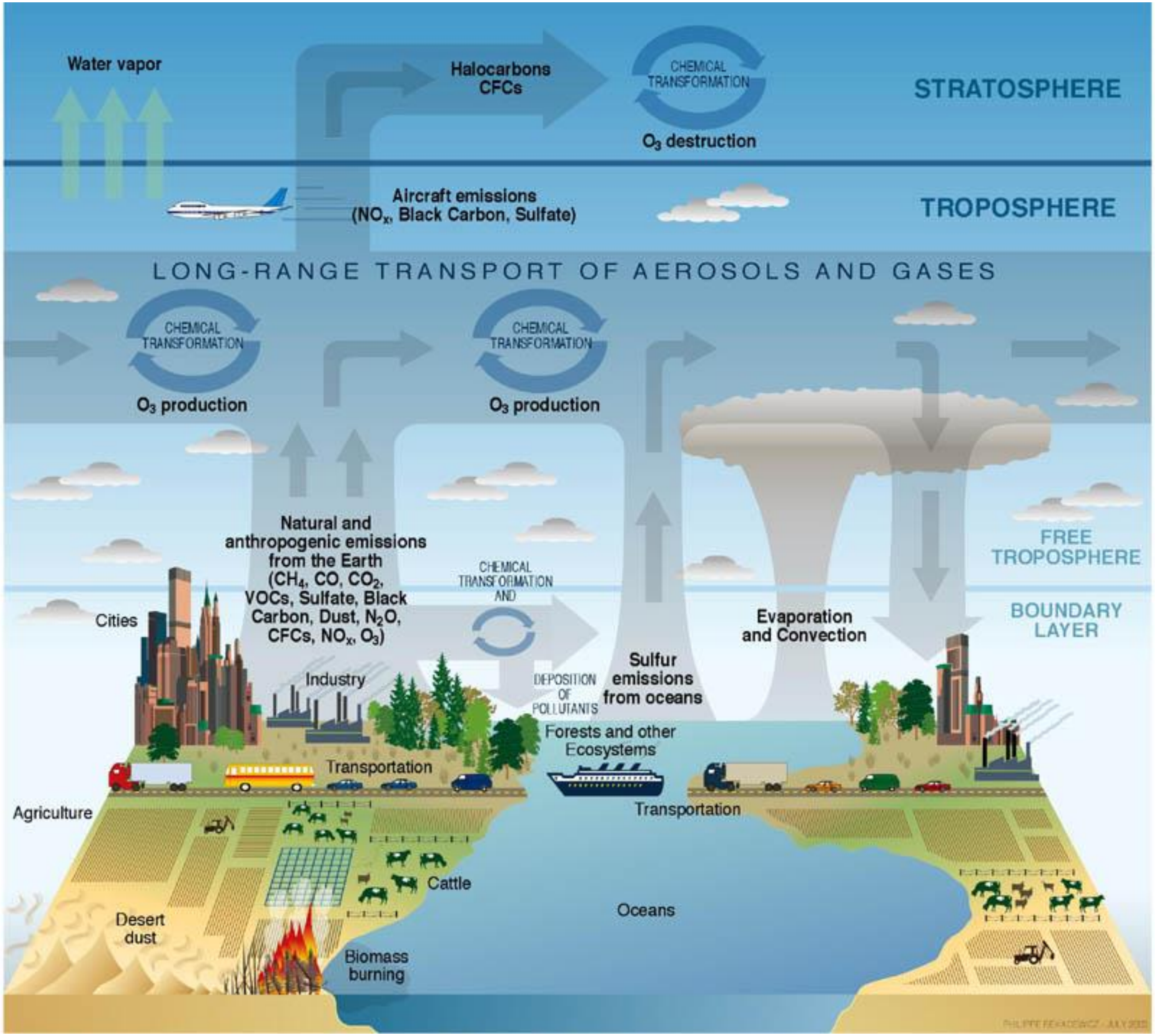
Natural Sources of Organic Compounds

Earth 281

NATURAL SOURCES OF ORGANIC COMPOUNDS

Some examples of organic compounds from natural sources:

A. biogenic trace gases
B. particulates/aerosols
C. halogenated hydrocarbons
D. petroleum hydrocarbons


Water vapor
Halocarbons
CFCs
CHEMICAL TRANSFORMATION
O_3 destruction
STRATOSPHERE
Aircraft emissions
(NO_x, Black Carbon, Sulfate)
TROPOSPHERE
LONG-RANGE TRANSPORT OF AEROSOLS AND GASES
CHEMICAL TRANSFORMATION
O_3 production
CHEMICAL TRANSFORMATION
O_3 production
Natural and anthropogenic emissions from the Earth (CH_4, CO, CO_2, VOCs, Sulfate, Black Carbon, Dust, N_2O, CFCs, NO_x, O_3)
CHEMICAL TRANSFORMATION AND
DEPOSITION OF POLLUTANTS
FREE TROPOSPHERE
BOUNDARY LAYER
Cities
Industry
Evaporation and Convection
Sulfur emissions from oceans
Forests and other Ecosystems
Transportation
Transportation
Agriculture
Cattle
Oceans
Desert dust
Biomass burning

A. BIOGENIC TRACE GASES

Biogenic VOCs (volatile organic carbon)

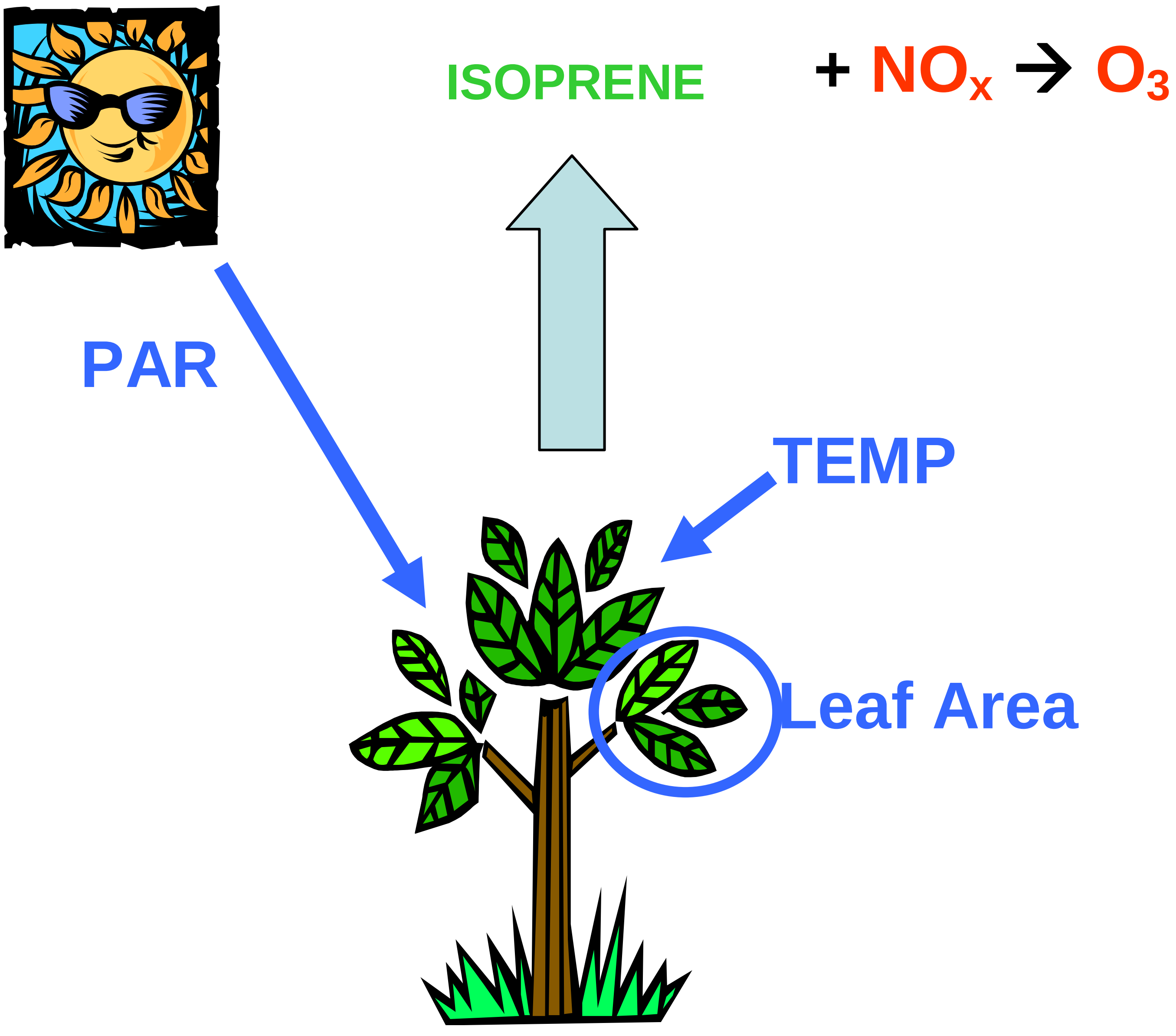
- overall, biogenic VOC emissions > anthropogenic VOC, but anthropogenic more significant in populated and industrial areas

  e.g.: Typical summer day in highly forested area of Texas (Wiedenmyer *et al.* 2001)

  biogenic VOC emissions ≥ 10 000 metric tons day^{-1}

  anthropogenic emissions ~ 2000 metric tons day^{-1}

- isoprene and monoterpenes are reactive VOCs which are emitted into the atmosphere by vegetation in large quantities
- estimated annual global emissions of non-methane biogenic VOCs = 438 Tg (10^{12} g)
- contribute to tropospheric ozone and secondary particle formation (→ smog)


ISOPRENE
+ NO_x → O_3
PAR
TEMP
Leaf Area

A. BIOGENIC TRACE GASES

Isoprene (C_5H_8)

Natural sources

- major emissions from woody plants (esp. deciduous trees such as oak, eucalyptus, aspen) to protect themselves from thermal stress

plantwerkz.blogspot.ca/

Table 8.1. Isoprene emission factors for plant species used in recent regional and global emission inventories. Standardized for bright sunlight (1000 µmol PAR m^{-2} s^{-1}) and 30°C (after Geron *et al.* 1994, Guenther *et al.* 1995, Simpson *et al.* 1995)

Genus	Isop.	Genus	Isop.	Genus	Isop.
	µg C g^{-1} (foliar dry weight) h^{-1}				
Casuarina[17]	70.0	*Caprinus*[13]	0.1	*Liriodendron*[41]	0.1
Eucalyptus[28]	70.0	*Carya*[14]	0.1	*Maclura*[42]	...
Liquidambar[40]	70.0	*Castanea*[15]	...	*Magnolia*[43]	0.1
Populus[56]	70.0	*Castanopsis*[16]	...	*Malus*[44]	...
Quercus[60]	70.0 (7.0; 70.0)[a]	*Catalpa*[18]	...	*Melia*[45]	0.1
Platanus[55]	35.0	*Cedrus*[19]	0.1	*Morus*[46]	0.1
Salix[64]	35.0	*Celtis*[20]	0.1	*Ostrya*[48]	...
Serenoa[67]	35.0	*Cercis*[21]	0.1	*Oxydendrum*[49]	0.1
Nyssa[47]	14.0	*Chamaecyparis*[2]	0.1	*Paulownia*[50]	...
Picea[52]	14.0 (1.8; 3.5)[a]	*Citrus*[23]	0.1	*Persa*[51]	0.1
Robinia[62]	14.0	*Cornus*[24]	0.1	*Pinus*[53]	0.1
Sabal[63]	14.0	*Cotinus*[25]	...	*Planera*[54]	...
Washingtonia[75]	14.0	*Crataegus*[26]	...	*Prosopis*[57]	...
Abies[1]	0.1	*Diospyros*[27]	0.1	*Prunus*[58]	0.1
Acacia[2]	0.1	*Fagus*[29]	0.1	*Pseudotsuga*[59]	0.1
Acer[3]	0.1	*Fraxinus*[30]	0.1	*Rhizophora*[61]	0.1
Aesculus[4]	...	*Gleditsia*[31]	...	*Sapium*[65]	...
Ailanthus[5]	...	*Gordonia*[32]	...	*Sassafras*[66]	0.1
Aleurites[6]	...	*Gymnocladus*[33]	...	*Sorbus*[68]	...
Alnus[7]	...	*Halesia*[34]	...	*Taxodium*[69]	0.1
Amelanchier[8]	...	*Ilex*[35]	0.1	*Thuja*[70]	0.1
Asimia[9]	...	*Juglans*[36]	0.1	*Tilia*[71]	...
Avicennia[10]	0.1	*Juniperus*[37]	0.1	*Tsuga*[72]	0.1
Betula[11]	0.1	*Laguncularia*[38]	0.1	*Ulmus*[73]	0.1
Bumelia[12]	...	*Larix*[39]	...	*Vaccinium*[74]	0.1

Emission factors are given in µg C g^{-1} (foliar dry weight) h^{-1}; Isop.: isoprene;

a: Factors used by Simpson *et al.* (1995). *Quercus*: 7.0 = Mediterranean area; 70.0 = other areas; *Picea*: 1.8 = majority of spruce forest; 10 = *P. sitchensis* (United Kingdom, Denmark, the Netherlands).

Common names: 1 Fir, 2 Acacia, 3 Maple, 4 Buckeye, 5 Ailanthus, 6 Tung-Oil Tree, 7 European Alder, 8 Serviceberry, 9 Pawpaw, 10 Black Mangrove, 11 Birch, 12 Gum Bumelia, 13 Hornbeam, 14 Hickory, 15 Chestnut, 16 Chinquapin, 17 Australian Pine, 18 Catalpa, 19 Deodar Cedar, 20 Hackberry, 21 Redbud, 22, Port-Orford Cedar, 23 Orange, 24 Dogwood, 25 Smoke Tree, 26, Hawthorn 27 Persimmon 28 Eucalyptus, 29 American Beech, 30 Ash, 31 Honeylocust, 32 Loblollybay, 33 Kentucky Coffee Tree, 34 Silverbell, 35 Holly, 36 Black Walnut, 37 Eastern Red Cedar, 38 White Mangrove, 39 Larch, 40 Sweetgum, 41 Yellow Popular, 42 Osage-Orange, 43 Magnolia, 44 Apple, 45 Chinaberry, 46 Mulberry, 47 Blackgum, 48 Hophornbeam, 49 Sourwood, 50 Paulowina, 51 Redbay, 52 Spruce, 53, Pine, 54 Water Elm, 55 Sycamore, 56 Aspen, 57 Mesquite, 58 Cherry, 59 Douglas-Fir, 60 Oak, 61 Red Mangrove, 62 Black Locust, 63 Cabbage Palmetto, 64 Willow, 65 Chinese Tallow Tree, 66 Sassafras, 67 Saw Palmetto, 68 Mountain Ash, 69 Cypress, 70 Western Cedar, 71 Basswood, 72 Eastern Hemlock, 73 American Elm, 74 Blueberry, 75 Fan Palm.

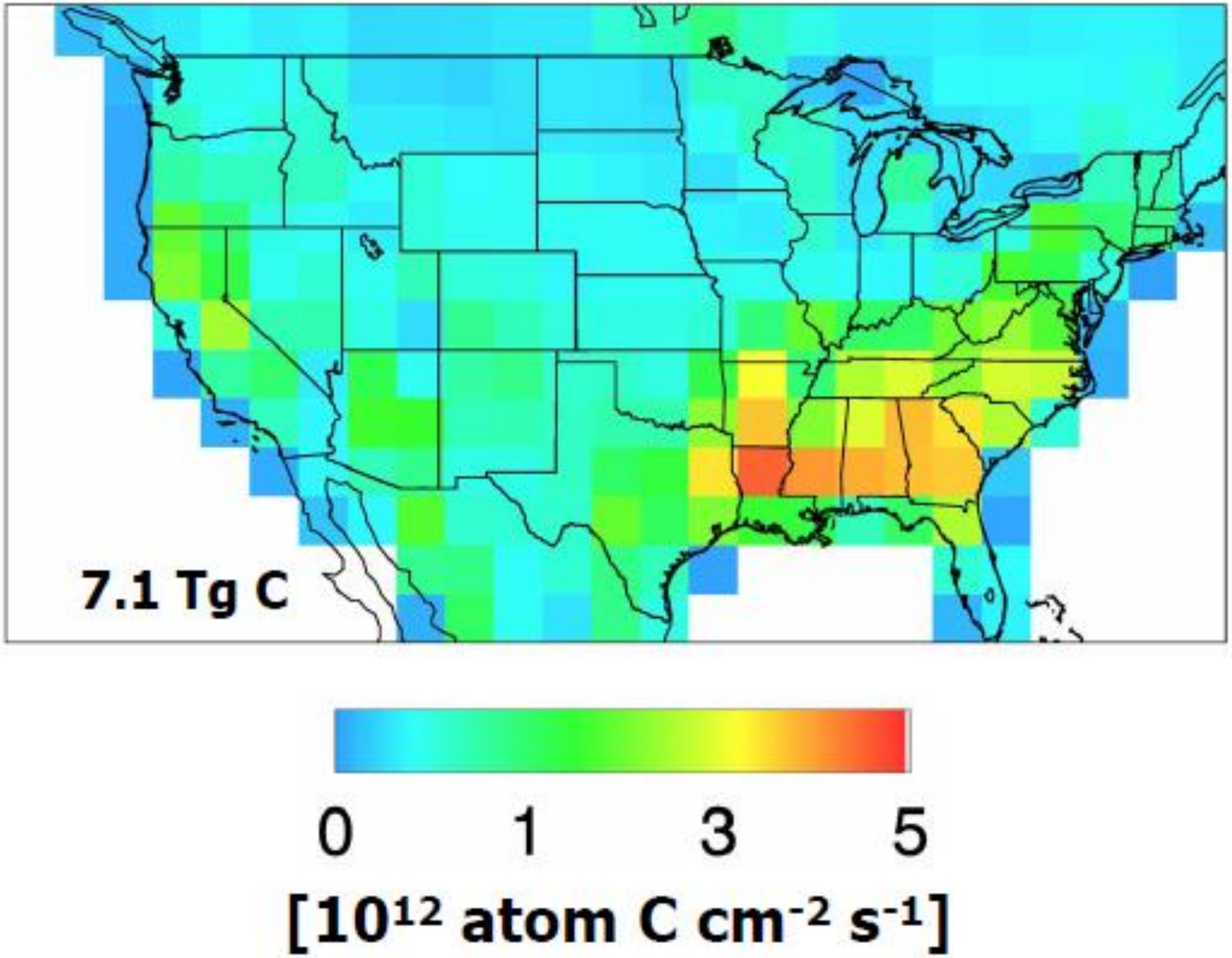
A. BIOGENIC TRACE GASES

Isoprene (C_5H_8)

Natural sources

- very minor emissions from microbes, animals (incl. human breath) and aquatic organisms
- temperature dependent. Therefore higher emissions during day vs. night, summer vs. winter, warm climates vs. cold climates
- woody landscapes cover 43% of terrestrial land surface and contribute to 77% to globally emitted isoprene (50% of which are emitted by tropical forests)

Global Isoprene Emissions – July 1996



[from Paul Palmer]

A. BIOGENIC TRACE GASES

Isoprene (C_5H_8)

Anthropogenic sources

- biomass burning, wood pulping, car exhaust

Health Effects

- tropospheric ozone formation → respiratory and cardiovascular effects, allergy exacerbation
  - isoprene reacts with the OH radical and then with NO_x (primarily from anthropogenic sources) to produce bad ozone (smog)

www.theguardian.com/

A. BIOGENIC TRACE GASES

Monoterpenes (general formula $(C_5H_8)_2$)

Examples – a-pinene, b-pinene, D_3-carene, limonene, sabinene, camphene

mastergarden.wordpress.com/

Natural sources

- mainly coniferous forests
- also temperature dependent

Health Effects

- particulates (aerosol) formation → respiratory and cardiovascular effects, allergy exacerbation
  - terpenes react with ozone, OH and NO_3 radicals to produce particulates that contribute to air pollution

A. BIOGENIC TRACE GASES

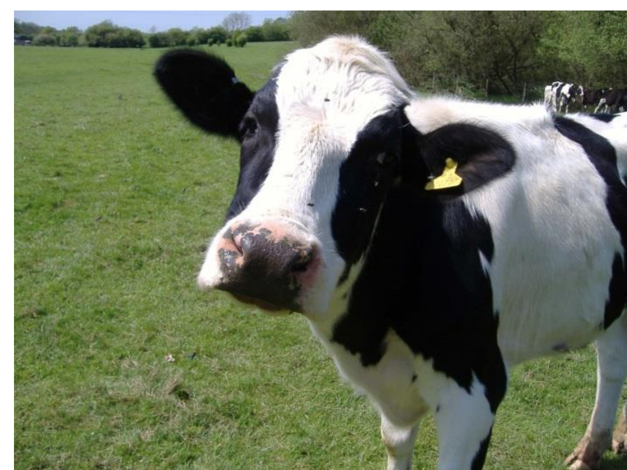
Methane (CH_4)

Natural sources

- natural sources ~40% of global methane emissions
- wetlands, termites, ocean, gas hydrates [Table]
- methanogenic bacteria – sediments, wetland soils, landfills, guts of animals (eg. termites and ruminants)
- plants do not produce CH_4, but CH_4 may be transported from sediments through plant roots and escape into atmosphere from leaves and/or shoots

www.ndsu.edu/

blogs.davenportlibrary.com/



www.saawinternational.org/

A. BIOGENIC TRACE GASES

Methane (CH_4)

Anthropogenic sources

- anthropogenic sources ~60% of global methane emissions
- landfills, fossil fuel production, animal husbandry (enteric fermentation in livestock and manure management), rice cultivation, biomass burning

www.infrastructurene.ws/

yakumosworld.aminus3.com/

A. BIOGENIC TRACE GASES

Methane (CH_4)

Health Effects

- tropospheric ozone formation → respiratory and cardiovascular effects
- greenhouse gas → global warming
  - atmospheric residence time ~10-12 years, therefore a global concern

Estimated sources of methane (Houweling *et al.*, 1999)

	Tg CH_4 yr^{-1}
Natural	**290**
Wetlands (incl. rice)	225
Ocean	20
Termites	15
CH_4 hydrate	5
Anthropogenic	**330**
Fossil fuel	110
Ruminants	115
Biomass burning	40
Landfills	40
Total Sources	**620**

B. PARTICULATES/AEROSOLS

Natural sources

- sea salt, mineral dust, pollens and spores, organic aerosols derived from biogenic VOCs

www.animhut.com/

Anthropogenic sources

- black carbon (soot), coal-burning, fly ash, organics derived from anthropogenic VOCs

www.nashvillescene.com/

Health Effects

- air pollution → respiratory and cardiovascular effects, allergy exacerbation

C. HALOGENATED HYDROCARBONS

Methylhalides

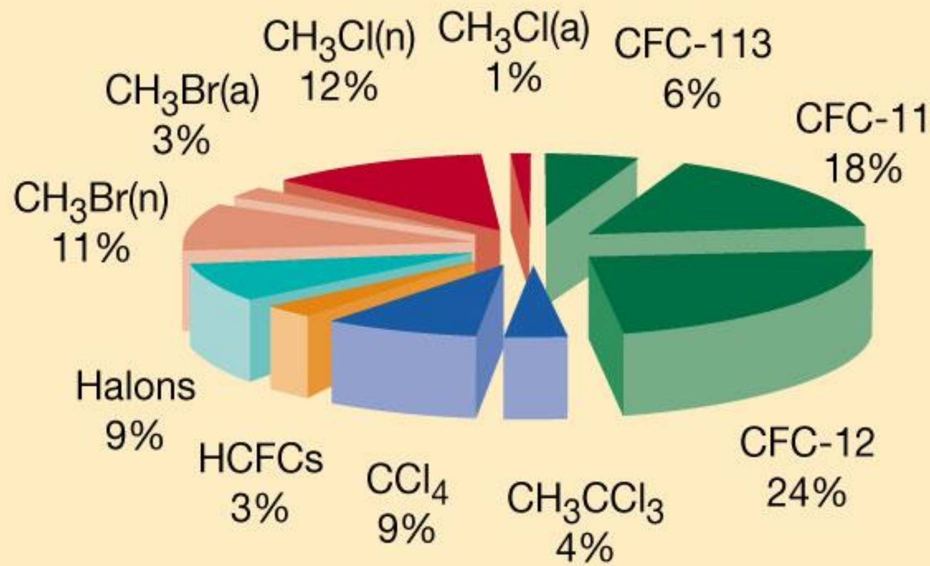
- CH_3Cl: methylchloride
- CH_3Br: methylbromide - largest source of bromine to atmosphere
- CH_3I: methyliodide

- produced in seawater and coastal areas and naturally emitted by marine plants and organisms

C. HALOGENATED HYDROCARBONS

Natural sources

- natural sources > anthropogenic sources



(n) = natural **(a) = anthropogenic**

Equivalent chlorine in ozone-depleting halogenated gases, 1999.

Halogens in the two methyl halides make up about a quarter of the equivalent chlorine from persistent organic compounds in the atmosphere.

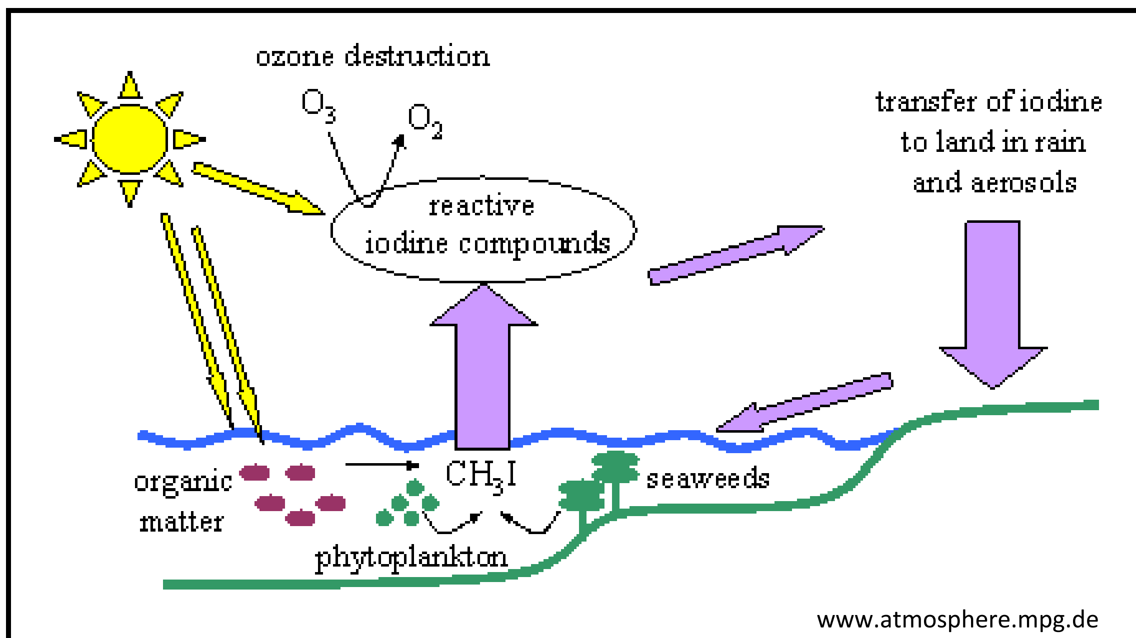
(Equivalent chlorine is the total number of chlorine atoms plus a weighting factor (50) multiplied by the total number of bromine atomscontributed by these compounds.)

From Butler, 2000 (Nature 403, 260-261)

C. HALOGENATED HYDROCARBONS

Natural sources

- ocean (halogen-rich seawater) and coastal zones (high primary productivity) are largest sources
- salt marshes only make up <0.1% of global surface area, but may be producing ~10% of global emissions of CH_3Br and CH_3Cl



C. HALOGENATED HYDROCARBONS

Natural sources

- sources of methyl halide production in coastal salt marshes
    - salt-tolerant plants (e.g. mangroves) [Photo]
    - algae (phytoplankton and seaweed)
    - fungi
    - soil microbes

MANGROVES IN CUBA (E.Williams)

C. HALOGENATED HYDROCARBONS

Anthropogenic sources

- CH_3Br – fumigation of soil, fruits/vegetables, timber
- CH_3Cl – formerly used as refrigerant but discontinued due to its toxicity

www.unfailingwaters.com/

www.colourbox.com/

C. HALOGENATED HYDROCARBONS

Health Effects

- stratospheric ozone depletion → UV exposure
- the key human health effects from exposure to UV-B include skin cancer, cataracts, and immunosuppression.
- other dermatological effects include severe photo-allergies and accelerated aging of the skin
- CH_3Br - respiratory, kidney, neurological effects
  - suspected carcinogen
- CH_3Cl - acute: central nervous system effects, paralysis, seizures, coma
  - chronic: birth defects

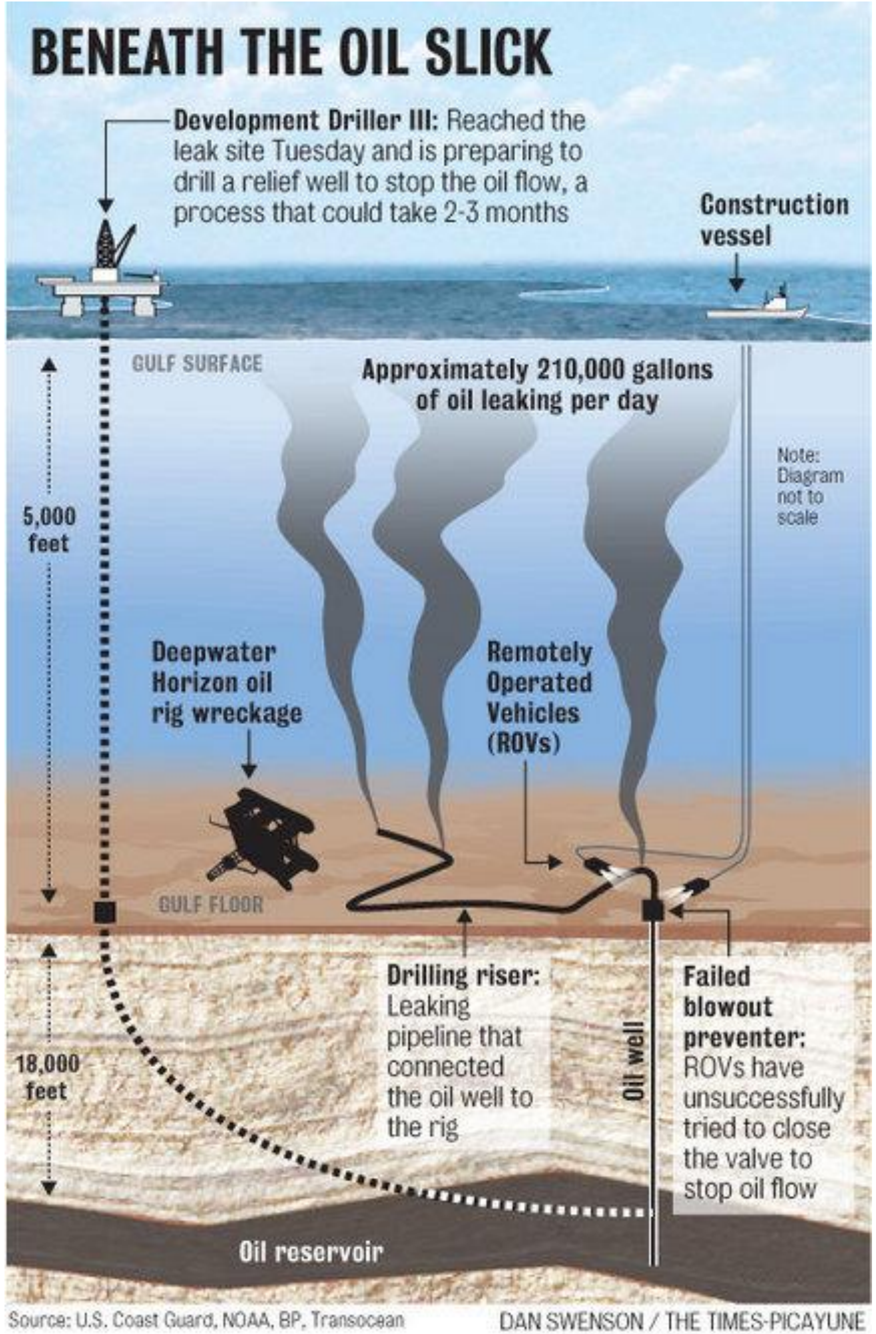
D. PETROLEUM HYDROCARBONS

- Chemicals present in petroleum hydrocarbons
  - Hydrocarbons: alkanes, naphthenes, aromatics (BTEX, PAHs)
  - Organic compounds of sulfur, oxygen, nitrogen
  - Metals, particularly vanadium nickel, iron, copper

www.theguardian.com/

D. PETROLEUM HYDROCARBONS

- How formed?
  - from Greek *petra* (rock) and Latin *oleum* (oil)
  - petrogenic – plant and animal debris incorporated into sedimentary rocks in marine environments. As the sedimentary rocks layer, they exert extreme heat and pressure to transforming the organic material into crude oil and natural gas



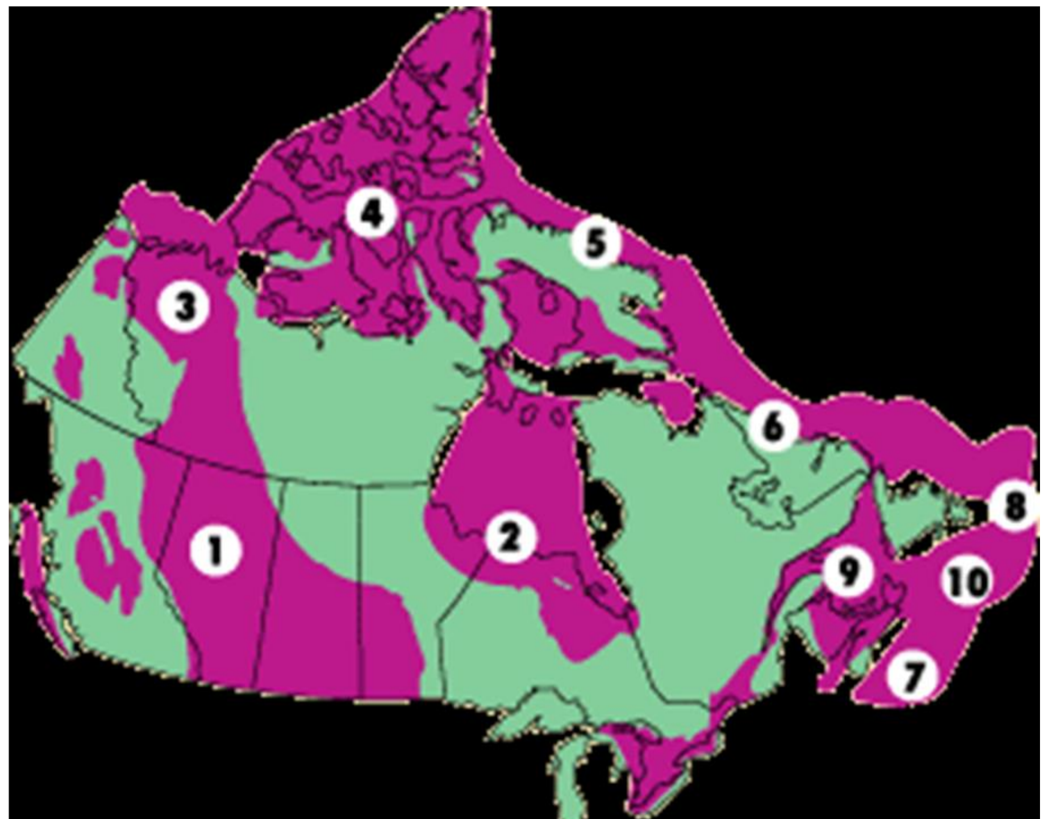
howstuffworks.com

Where found? Canadian deposits

Key:

1	Western Canada Sedimentary Basin (our primary source of oil)
2	Hudson Bay Basin
3	Mackenzie and Banks Basins
4	Canadian Arctic Basin
5	Baffin Bay
6	Labrador Sea Shelves
7	Scotian Shelf
8	Grand Banks
9	Anticosti
10	Maritimes Basins.

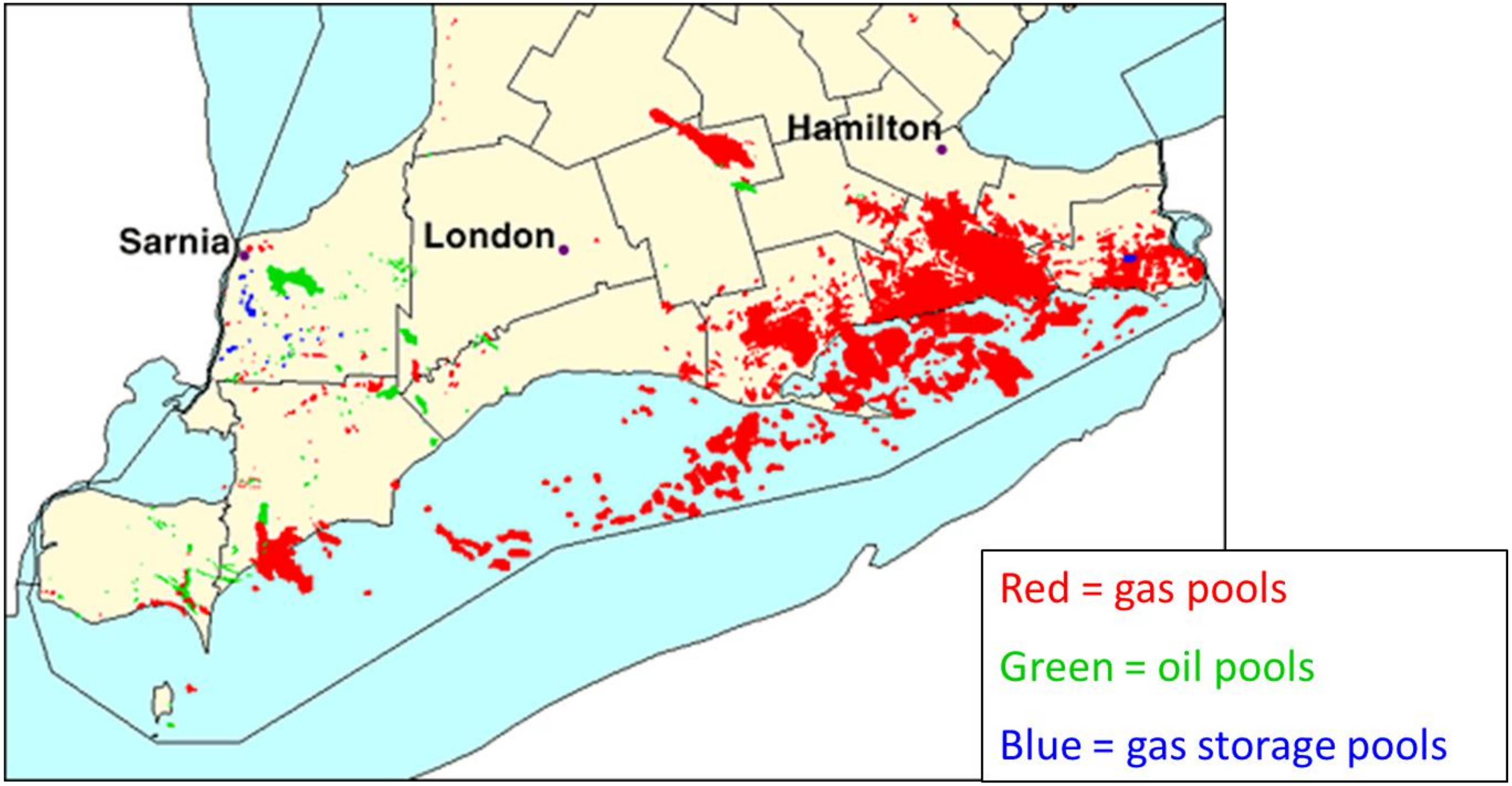
Major Canadian Deposits



Environment Canada (2005)

Where found? Southern Ontario pools

Map showing oil, natural gas and natural gas storage pools in southern Ontario. Some smaller natural gas pools occurring to the north of this area are not shown.



www.mnr.gov.on.ca/mnr/ogsr/resources2.htm

D. PETROLEUM HYDROCARBONS

- Natural seeps
- Petroleum hydrocarbons introduced naturally as oil and gas seepage
- ~200 natural underwater oil seeps have been identified around the world mixtures of crude oil, asphaltum (tar), natural gas and water

La Brea

www.naturalhistorymag.com/

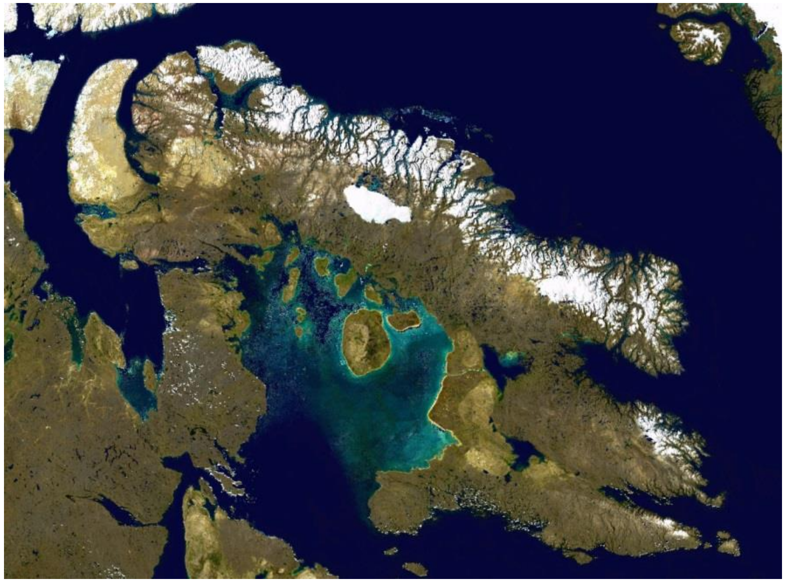
legionmagazine.com/

Oil Springs, Ontario

D. PETROLEUM HYDROCARBONS

- Types of seeps
  - Terrestrial springs and tar pits
    - Athabasca Oil Sands in Alberta
    - Orinoco Tar Sands in Venezuela
    - La Brea tar pits in California
  - Terrestrial gas seeps (e.g. The Chimera in Greece)
  - Marine carbonate seeps on continental shelves
  - Marine gaseous and liquid hydrocarbon seeps
    - off coasts of Labrador and Baffin Island
    - one of world’s largest: Caspian Sea in Republic of Azerbaijan
    - another of world’s largest: Santa Barbara County, California

wikimedia.org



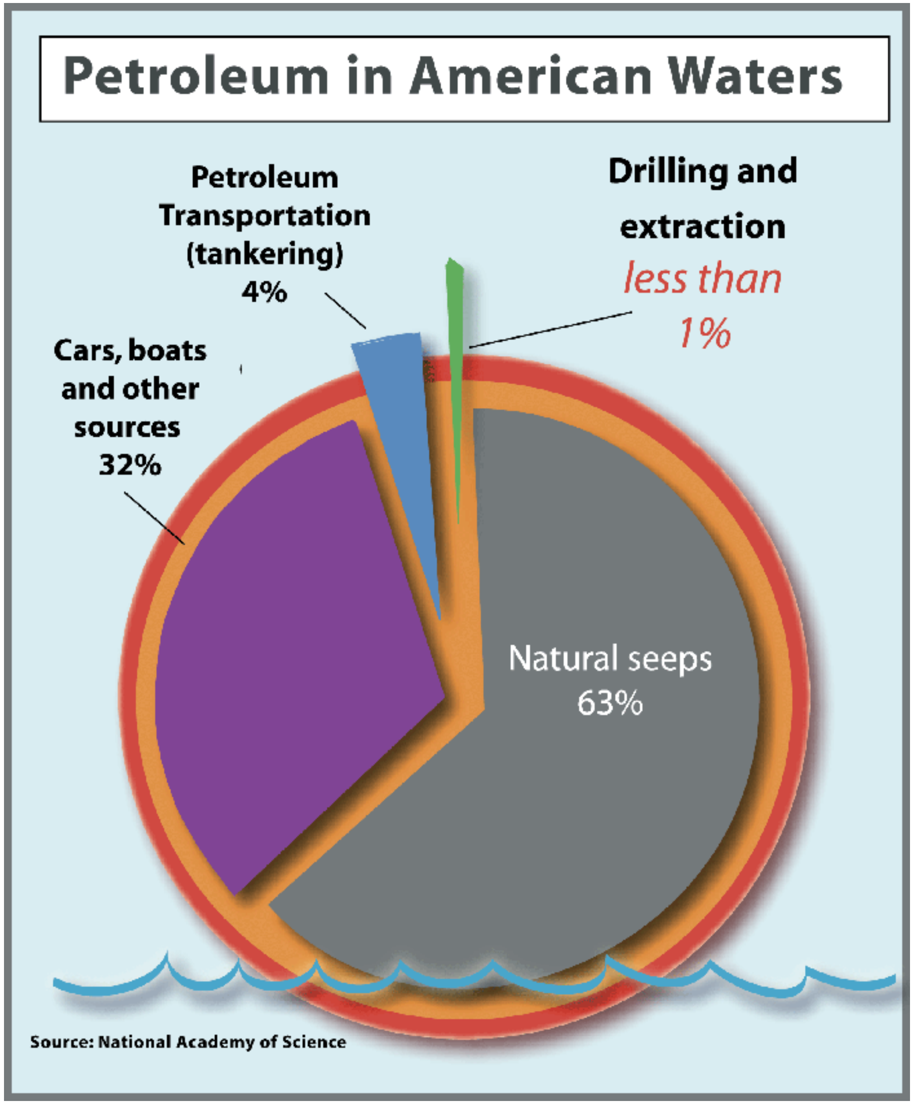
wikimedia.org

Athabasca Oil Sands
Labrador and Baffin Island
The Chimera, Greece

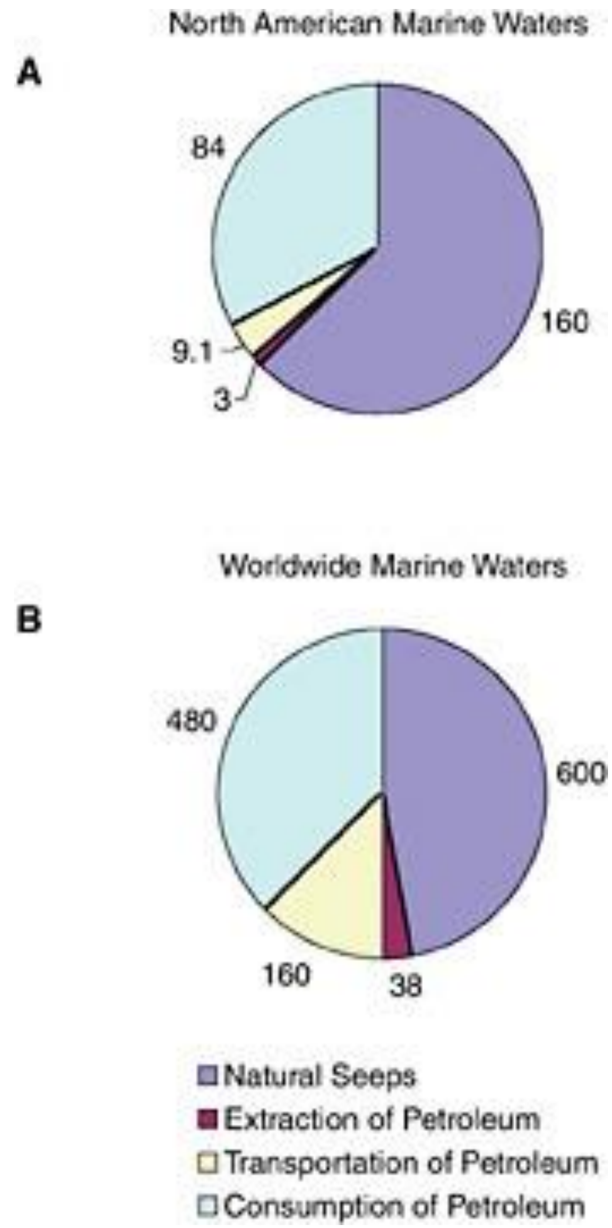
www.theguardian.com/

D. PETROLEUM HYDROCARBONS

- Significance
  - Have seeped naturally for millions of years
  - Human history
    - Huron Indians dipped buckets in pools of oil
    - Chumash Indians (California) used asphaltum to caulk their wooden canoes and waterproof their woven waterbottles
    - Yokut Indians (California) used asphaltum inlaid with shells to decorate bowls, jewelry, knives etc. Shamans painted face with oil, believing it to have supernatural powers.
    - early settlers – waterproofing, lubrication, lamp oil
  - Substantial releases - ~60% of emissions to NA oceans [Figure]



Oil in the Sea III, NRC (2002)

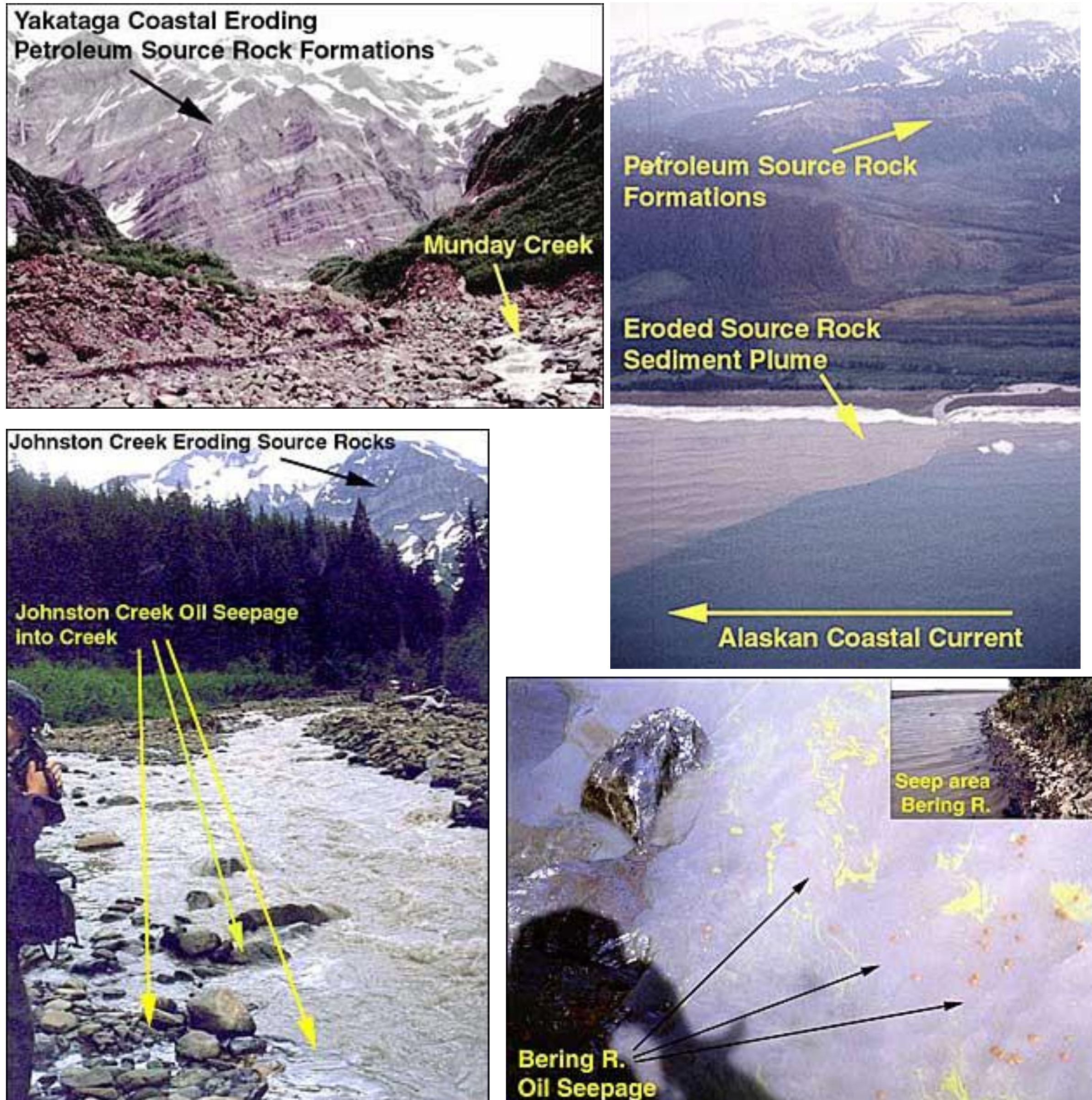


D. PETROLEUM HYDROCARBONS

- Examples
  - NWT and Alberta – Mackenzie River
    - Naturally occurring PAHs from oil seeps and/or bitumen present
  - Alaska – Prince William Sound [Photos]
    - Location of Exxon Valdez oil tanker spill in 1989
    - Substantially greater natural releases of oil in sediments compared to oil released from Exxon Valdez
    - Source is eroding shales and natural oil seepage
  - California – Santa Barbara County [Photos]
    - Seepage rates may be on order of 100 barrels/day
    - Deposits of oil residues ("tar balls") along coastline

Prince William Sound, Alaska

Oil seeps out of exposed faults at the base of a hill next to the river.



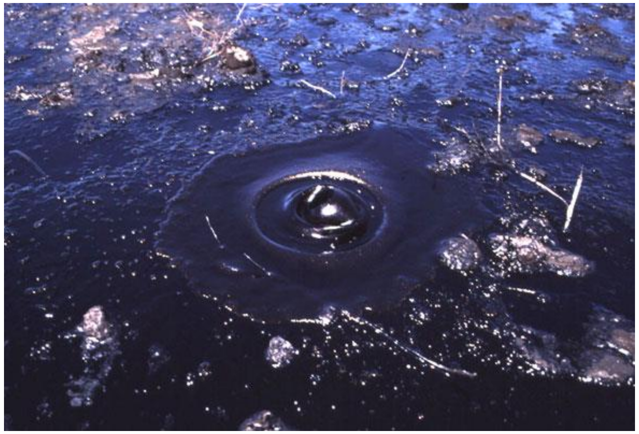
academic.bowdoin.edu/faculty/D/dpage/alaskan_oil

Petroleum seep on a beach, California

Tar balls (weathered oil) on a beach

Santa Barbara County, California

Petroleum seeps along Hwy 150, Ventura County, CA.



Petroleum seep with oil and gas rising to the surface

Photos by S. Mulqueen
www.consrv.ca.gov/dog/kids_teachers/seeps/index.htm

D. PETROLEUM HYDROCARBONS

- Ecological Impacts
  - Natural seeps are a source of chronic, low-level stress to aquatic organisms; less intense than the acute effect of oil spills
  - Chemosynthetic communities – some organisms gain energy from methane produced at concentrations that would be toxic to most organisms (e.g. mussels in Gulf of Mexico) [Photo]

Chemosynthetic Communities in the Gulf of Mexico

oceanexplorer.noaa.gov/explorations/02mexico/background/communities/communities.html)

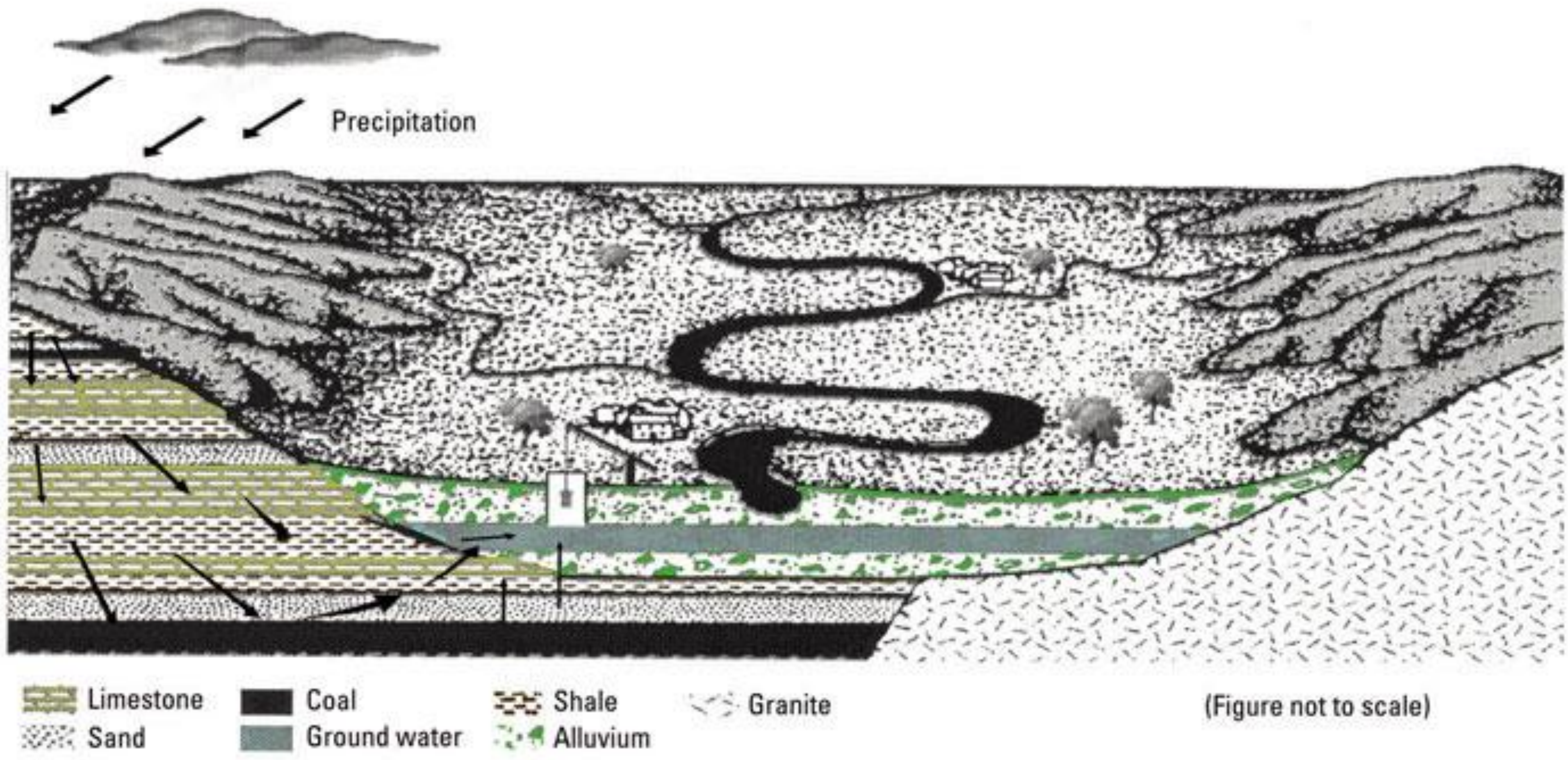
A small bush of tubeworms. When tubeworm bushes are young, only endemic species of animals can colonize them. The presence of the mussels *(Bathymodiolis childressi)* in the center of the bush means that methane is seeping just below.

D. PETROLEUM HYDROCARBONS

- Health impact
  - Direct
    - many components toxic or carcinogenic, dermatitis, problems associated with inhalation of volatile components
    - Shaw (one of first to drill in Ontario) died from breathing noxious gases while cleaning his well
    - Gases H_2S, CO, CO_2, CH_4, etc

D. PETROLEUM HYDROCARBONS

- Health impact
  - Direct continued
    - BEN - Balkan Endemic Nephropathy (kidney disease) and renal pelvic cancer
      - rural regions of Bulgaria, Romania, Serbia, Croatia and Bosnia
      - Groundwater flow through shallow lignite coals dissolves complex hydrocarbons and used as drinking water [Figure]
      - In US, greatest cancer mortality rates from kidney and renal pelvic cancer are Alaska, Maine, North and South Dakota and Minnesota, all with extensive lignite or peat deposits and considerable rural populations. Coincidence?



Tatu et al. 1998, Environmental Health Perspectives 106 (11)

Figure 4. Schematic representation of the hypothesized weathering of Pliocene lignites proximal to or underlying the BEN foci located in alluvial valleys, and of the transportation process (indicated by arrows) of the leached organic compounds into the ground and well water. Adapted from Feder et al.

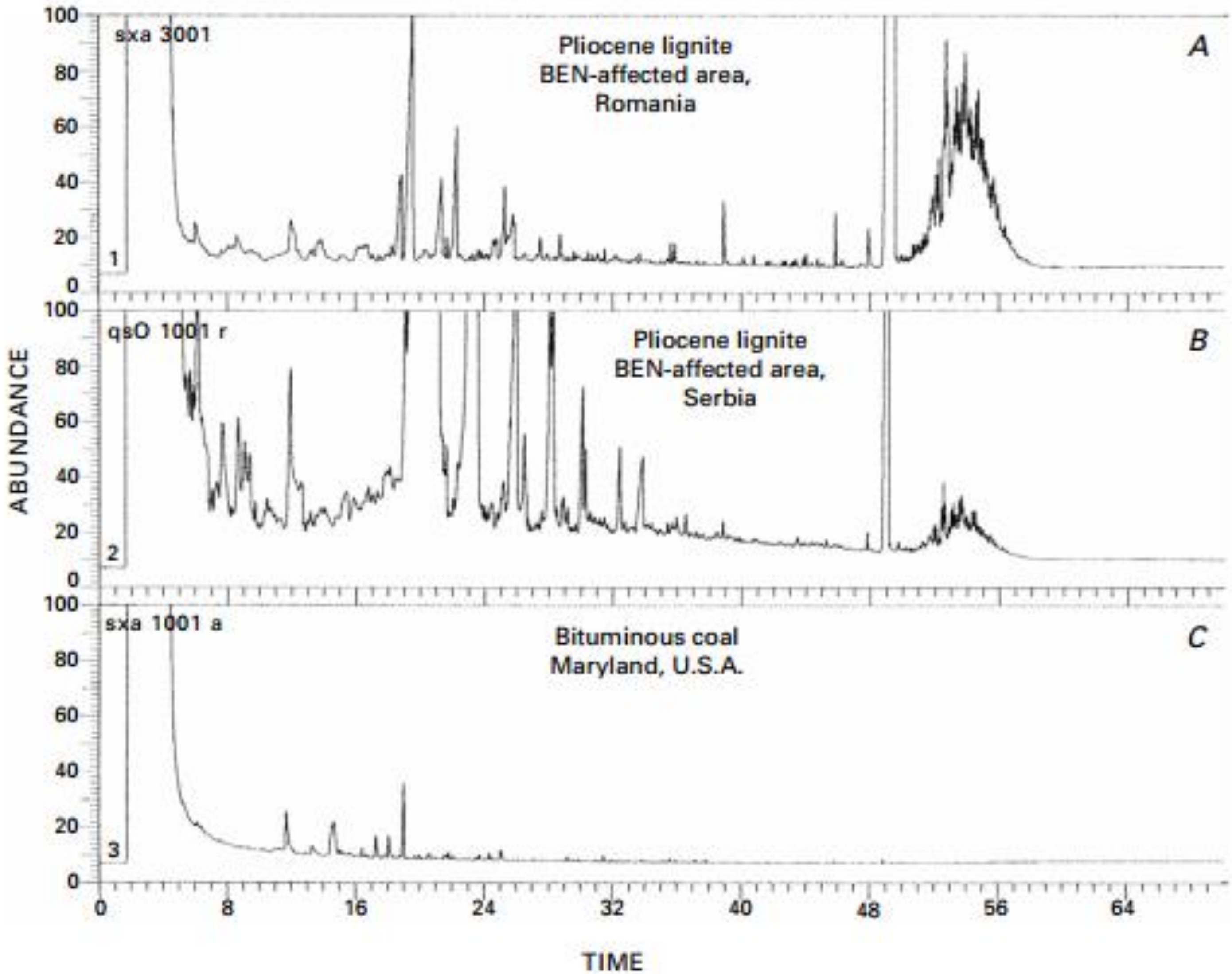


Figure 6. Gas chromatograms of laboratory water extracts of Pliocene lignites from two BEN-affected areas—Romania (*A*) and Serbia (*B*)—and of a bituminous coal from Maryland, U.S.A. (*C*). Peaks indicate the presence of potentially toxic organic compounds.

Skinner 2003

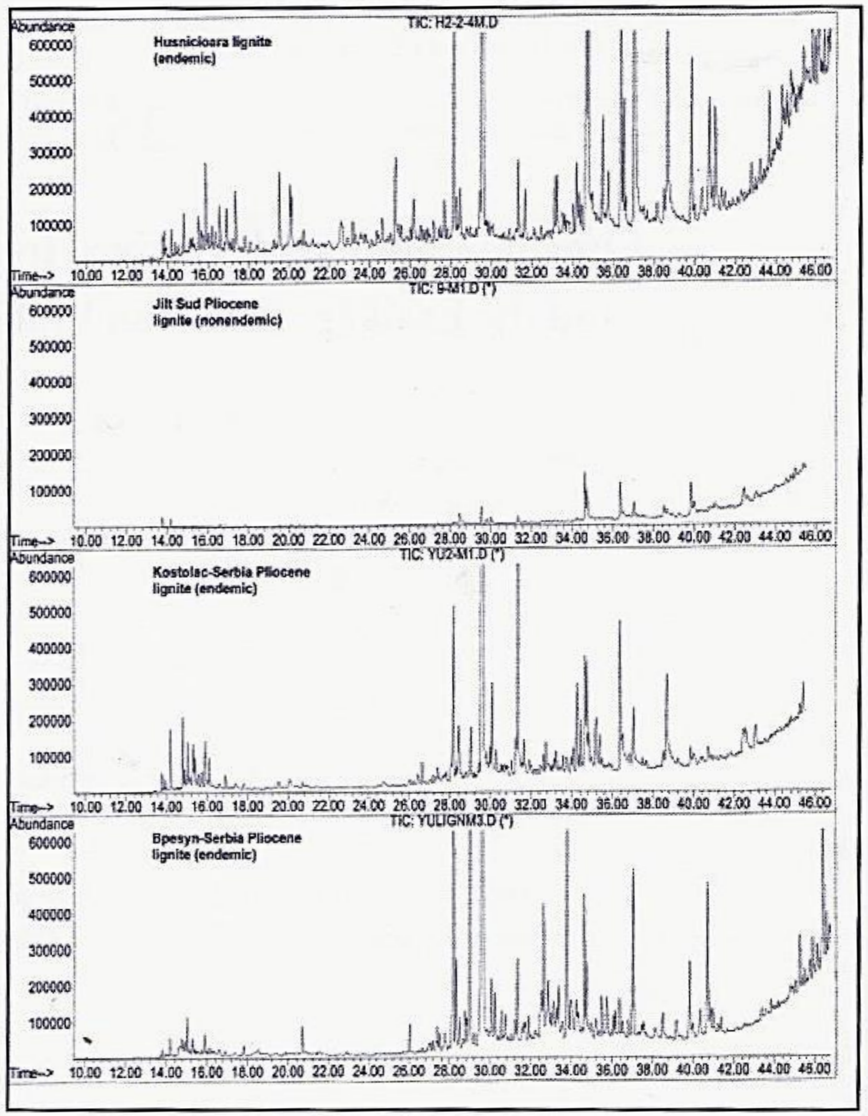


Figure 26.1: Mass spectra of three BEN endemic area Pliocene lignite samples and one nonendemic area lignite (Jilt Sud) of similar rank and age; 16 nonendemic lignites analyzed (see text) give similar spectra to Jilt Sud sample but are not shown.

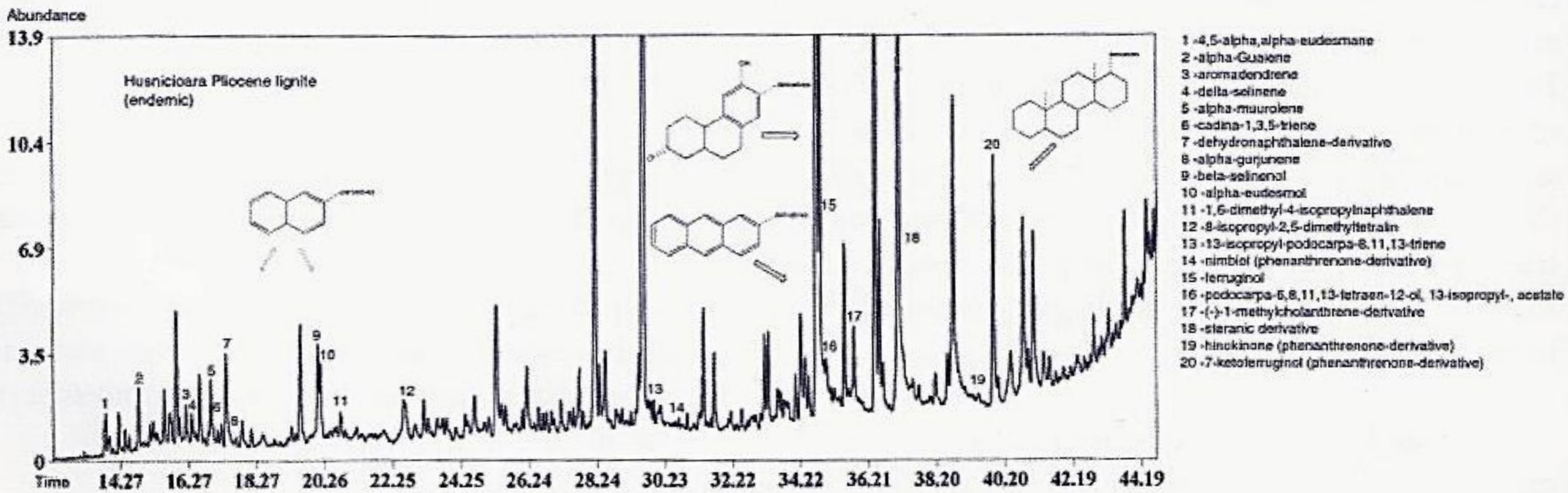


Figure 26.2: Mass spectra of an endemic Pliocene lignite with most of the compounds that could be identified labeled. The species are similar to those in the spectra illustrated in Figure 26.1.

D. PETROLEUM HYDROCARBONS

- Health impact
  - Indirect
    - Food chain (eg. bioaccumulation in fish and seafood)
    - Contribute to tropospheric ozone formation