A Scientific Critique of the Proposed Federal Clean Water Act Mercury Total Maximum Daily Load for the State of Florida: Appendix I- The General Mercury Problem

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Abstract

Section 303(d)(1)(C) of the U,S. Federal Clean Water Act (CWA) mandates that water quality-impaired waters be restored to fisheries and recreational uses by calculating a Total Maximum Daily Load (TMDL) based on the capacity of the receiving water to assimilate the pollutant so as not to exceed the applicable Water Quality Standard for each impairing pollutant. The TMDL has to quantify all controllable and uncontrollable point and nonpoint sources of pollution within a mass balance framework, including natural background, and has to take into account seasonal variation in the assimilative capacity with a margin of safety sufficient to compensate for any lack of knowledge about the loading rate-concentration relationship in the receiving water under seasonally appropriate conditions. The TMDL provision of the CWA anticipates a waterbody-specific TMDL, but Florida is proposing a statewide approach, because most of the controllable mercury sources are air emissions sources that originate outside of Florida, and wet and dry atmospheric deposition of inorganic mercury from these regional, continental, and global sources is relatively uniform across the state. The proposed approach requires an 86% reduction to achieve a Water Quality Target equal to the Federal Environmental Protection Agency's Water Quality Criterion of 0.3 ppm methylmercury as total mercury in fish flesh. However, the proposed mercury TMDL for Florida omits an important background source and a substantial controllable nonpoint source. It also sacrifices the most methylmercury-susceptible waters. This paper summarizes the scientific and administrative deficiencies of Florida's statewide approach and strategy for mercury source reduction and proposes the analysis, synthesis, and integration of research, monitoring, and modeling to close the gap between Florida's proposed approach and sound science constrained by the administrative requirements of the CWA.

Introduction

- Methylmercury (MeHg) contaminates Florida’s fresh and salt water sport and commercial fish species to levels necessitating the issuance of consumption advisories to protect the public health.
- Fishable uses of waters where advisories are in effect are mercury-impaired.
- This condition triggers mandatory mercury source reduction under Federal Clean Water Act (CWA) Section 303(d)(1)(C), the Total Maximum Daily Load (TMDL).

Introduction

- The TMDL is the capacity of the most susceptible waterbody in the watershed to assimilate the pollutant's mass loading rate at the pollutant's WQS, taking into account seasonal variation in sources and conditions and with an adequate margin of safety to offset all uncertainties.
- Under Federal Court Order the U.S. Environmental Protection Agency (USEPA) Region 4 was to implement water quality-based source controls for all impaired waters by 09/30/11 using TMDL process.

Introduction

- Most of the mercury causing fresh and salt water impairment is now being imported regionally, continentally, and globally from air emissions sources outside CWA control and many outside of the USA beyond the reach of the Federal Clean Air Act (CAA).
- This necessitates a broader approach to restore mercury-impaired waters than the traditional focus on point source controls and nonpoint source best management practices (BMPs).

Introduction

- This is the basis for a statewide approach to mercury TMDL calculation and implementation, already approved by USEPA for other states, e.g., Minnesota.
- FL is proposing to reduce the MeHg concentrations in top-predator sport fish by 60%, which, because of a 30% uncontrollable natural background mass loading rate, requires an 86% reduction of mercury mass emissions from controllable air sources at every scale.

Introduction

- … even though there is no legal basis for THg air emissions limits in CAA permits based on a CWA Hg TMDL.
- This is a critique of the administrative and scientific deficiencies supporting Florida’s proposed statewide mercury TMDL, not the need for mercury source reduction in general or to restore and protect mercury-impaired waters in the USA or worldwide.
- This section of the presentation focuses on discussing in more detail the general mercury problem.

Definitions

TMDL = Total Maximum Daily Load

the mass loading rate to a receiving water that results in the attainment of the pollutant's WQS under seasonally appropriate design low assimilative capacity conditions

LA = Load Allocation

the sum of all pollutant mass loading rates from natural background and all uncontrollable point and nonpoint sources, including contaminated ground-water and sediments not scheduled for remediation

MOS = Margin of Safety (MOS)

a reduction in the TMDL to compensate for the uncertainties in the load-conc. relationship

WLA = Waste Load Allocation

= TMDL – MOS – LA

the equitable distribution of the remaining unused assimilative capacity to point and controllable nonpoint sources under the authority of the CWA

Appendix I: The General Mercury Problem

The Global Hg Problem

<u>Extent of the Mercury (Hg) Problem</u>

- Human fish consumption health advisories are extant worldwide.
- Some fish-eating wildlife popsulations are at local risk of reproductive failure, but general risk grows.
- Monomethylmercury (MeHg) is the problem
- MeHg is produced primarily from new inorganic Hg (IHg) in wet and dry atmospheric deposition, …

The Global Hg Problem

Extent of the Mercury (Hg) Problem

- … primarily in sediment virtually devoid of dissolved oxygen (DO) by oxygen-avoiding (anaerobic) natural bacteria.
- Dryout and rewetting of soil and sediment with high legacy THg levels from historical sources may contribute to short-term MeHg anomalies, esp. with excess sulfate.
- Global warming may exacerbate Hg problem, because in some waters net IHg methylation increases with temperature.

The Global Hg Problem

<u>Origin of the Mercury Problem Awareness</u>

- In the early 1950s, Chisso Corporation began to discharge wastewater containing mercury to Japan’s Minamata Bay.
- By the late 1950s, activists had alerted journalists to an outbreak of confused adults and deformed, paralyzed, and cognitively impaired children consuming MeHg-contaminated fish from the bay.
- Accidental poisonings that followed in Iran and elsewhere confirmed the public health risks from exposure to MeHg in fish.

The Global Hg Problem

Hg Sources and Air Transport

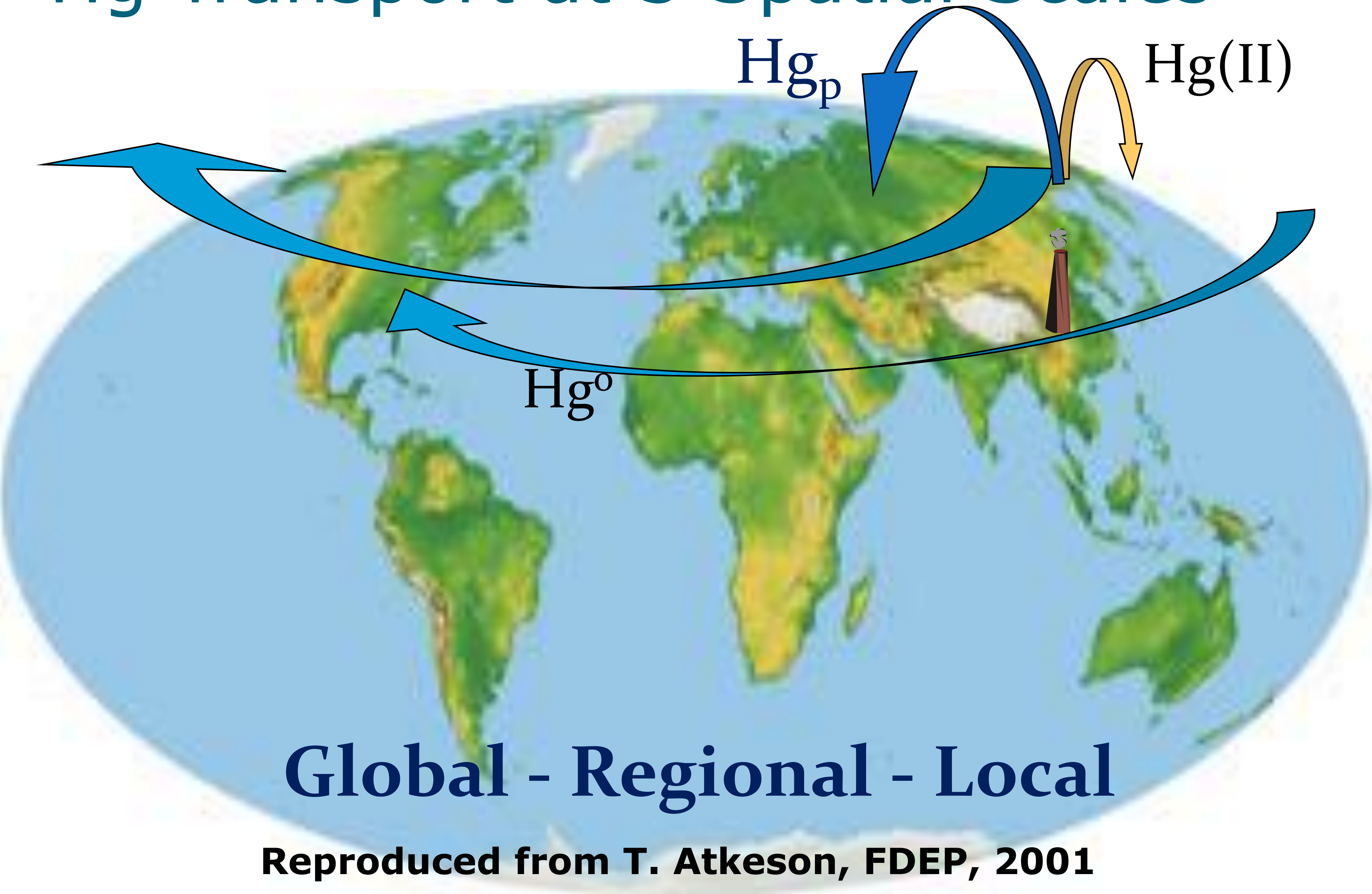
- Significant historical sources, e.g., gold mining, uranium processing and chlor-alkali plants, medical and dental offices, anti-fungal paints, battery production and recycling, and solid, medical and hazardous waste incinerators.
- Significant sources today, e.g., coal-fired power plants and boilers, cement kilns, crematoria w/o mercury fillings separation, solid waste incinerators w/o Hg source separation, land-applied biosolids and landfill flares.

The Global Hg Problem

Hg Sources and Air Transport

- Elemental mercury, $Hg(0)^{0}$, particle-bound inorganic mercury, $Hg(II)_p^{2+}$, and gas-phase $X\text{-}Hg(II)^{2+}$, a.k.a, reactive gaseous mercury, RGM, are emitted by combustion sources, esp. coal-fired power plants.
- RGM has a high affinity for water, soil, and leaf surfaces and deposits locally, particle-bound $Hg(II)_p^{2+}$ deposits regionally, but $Hg(0)^{0}$ transports and deposits globally.

Hg Transport at 3 Spatial Scales



Global - Regional - Local

Reproduced from T. Atkeson, FDEP, 2001

Global Hg Emissions Densities

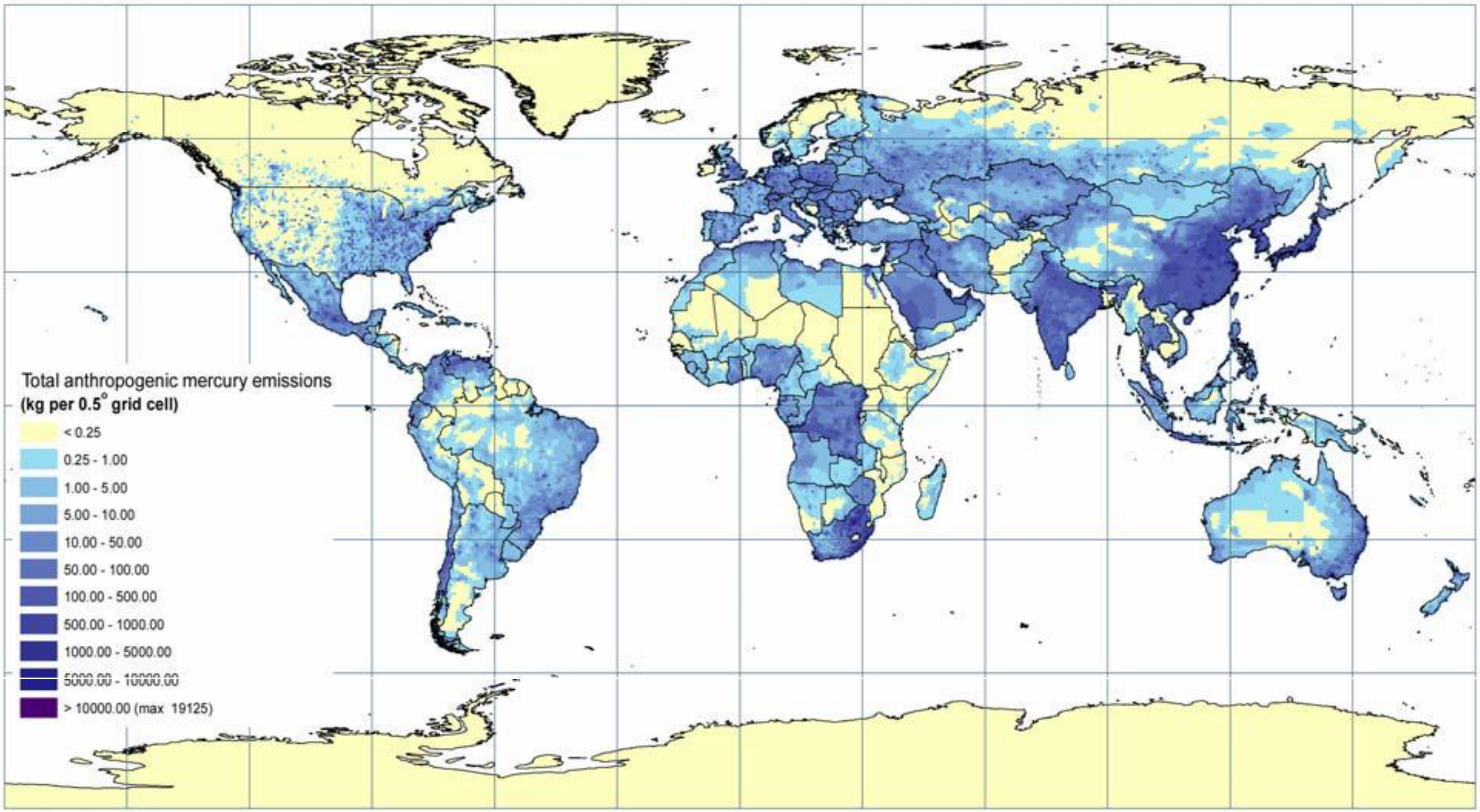


Figure 1. Spatial distribution of global anthropogenic mercury emissions (2000). from Pacyna et al. (2005, 2006) and Wilson et al. (2006)

The Global Hg Problem

Hg Sources and Air Transport

- $Hg(0)^{0}$ in the global pool is then converted to X-$Hg(II)^{2+}$ in air, by rxns with natural oxidizers, esp. bromine species, in the upper troposphere.
- Problem is decreasing in the USA as coal-fired power plants are retrofitted or decommissioned …
- … but increasing globally as more coal-fired power plants come on-line in India and China.
- Watershed soils and water body sediments retain excess $Hg(II)^{2+}$ concs. from pre-regulation local, regional, and global "legacy" Hg sources, but not necessarily in a form that is (bio)available to methylating bacteria.

The Global Hg Problem

Mercury Aquatic Bigeochemistry

- $Hg(II)^{2+}$ → $CH_3Hg(II)^{+}$ in oxygen-free (anoxic) sediment, primarily by anaerobic sulfate-reducing bacteria (SRB) and iron-reducing bacteria (IRB)
- $Hg(II)^{2+}$ → $Hg(0)^{0}$ in anoxic sediment by microbiota
- $CH_3Hg(II)^{+}$ → $Hg(II)^{2+}$ in anoxic sediments primarily by acetogens and methanogens

The Global Hg Problem

Mercury Aquatic Bigeochemistry

- $Hg(II)^{2+} \rightarrow Hg(0)^{0}$ in water by sunlight with and without mediation by dissolved organic carbon (DOC)
- $CH_3Hg(II)^{+} \rightarrow Hg(0)^{0}$ or $Hg(II)^{2+}$ in water by sunlight w/ or w/o mediation by DOC
- The more bioaccumulative and toxic dimethylmercury, $(CH_3)_2Hg(II)^{0}$, is also a byproduct of anaerobic bacteria metabolism, but it is rapidly lost from aquatic ecosystems via natural processes

The Global Hg Problem

Mercury Aquatic Bioaccumulation

- $Hg(II)^{2+}$ and MeHg sorb (adsorb or absorb) to non-living (abiotic, e.g., sand, silt and clay) particles and living (microbiotic, e.g., viri, bacteria, diatoms, and green and blue-green algae) particles in competition with DOC and other precipitating counter ions, e.g., HS^-
- $Hg(II)^{2+}$ and MeHg adsorb (surface) or absorb (interior) and (bio)concentrate in microbiota at the base of the food chain with high surface area-to-volume ratios, esp. algae ~ 5,000 – 50,000 times

The Global Hg Problem

<u>Mercury Aquatic Bioaccumulation</u>

- Micro- and macrobiotic filter feeders bioaccumulate MeHg 2-7x algae preferentially over $Hg(II)^{2+}$, because MeHg readily passes gill & gut membranes
- Benthic macroinvertebrates that digest waste in surficial sediments bioaccumulate 0.5-3x MeHg in the surrounding sediment
- Small, medium, and large fish 2-7x MeHg in their microscopic, small-, and medium-sized prey

The Global Hg Problem

Mercury Terrestrial Bioaccumulation

- Mink & otter bioaccumulate 1.5-3x weighted average [MeHg] in their diet.
- Top-predator bird eggs 2-7x diet [MeHg]
- Their predators, e.g., eagles, 2-3x
- Alligators 2-7x diet [MeHg]
- Florida panther adults preying on otter, raccoons, juvenile alligators, and juvenile panthers bioaccumulated as much as 110 ppm THg as MeHg in fur (FPIC, 1989, ’91)

The Global Hg Problem

Mercury Exposure and Effects

- All mercury species interfere with brain development and function
- MeHg likely also interferes with endocrine system and chromosome separation in cell division by disrupting tubulin polymerization
- Toxicity to Humans: $(CH_3)_2Hg(II)^{\mathbf{0}}$ > $CH_3Hg(II)^{+}$ > $Hg(0)^{\mathbf{0}}$ > $Hg(II)^{2+}$
- Toxicity to Wildlife: generally same order

The Global Hg Problem

<u>Mercury Exposure and Effects</u>

- Bioaccumulation Potential in Aquatic Ecosystems: $(CH_3)_2Hg(II)^{\mathbf{0}}$ > $CH_3Hg(II)^+$ > Hg(0) > $Hg(II)^{\mathbf{2+}}$
- Persistence in Aquatic Ecosystems: $Hg(II)^{\mathbf{2+}}$ > $CH_3Hg(II)^+$ > $Hg(0)^{\mathbf{0}}$ > $(CH_3)_2Hg(II)^{\mathbf{0}}$
- Human Health Hazard: $CH_3Hg(II)^+$ >> $Hg(0)^{\mathbf{0}}$ >> $Hg(II)^{\mathbf{2+}}$ >> $(CH_3)_2Hg(II)^{\mathbf{0}}$

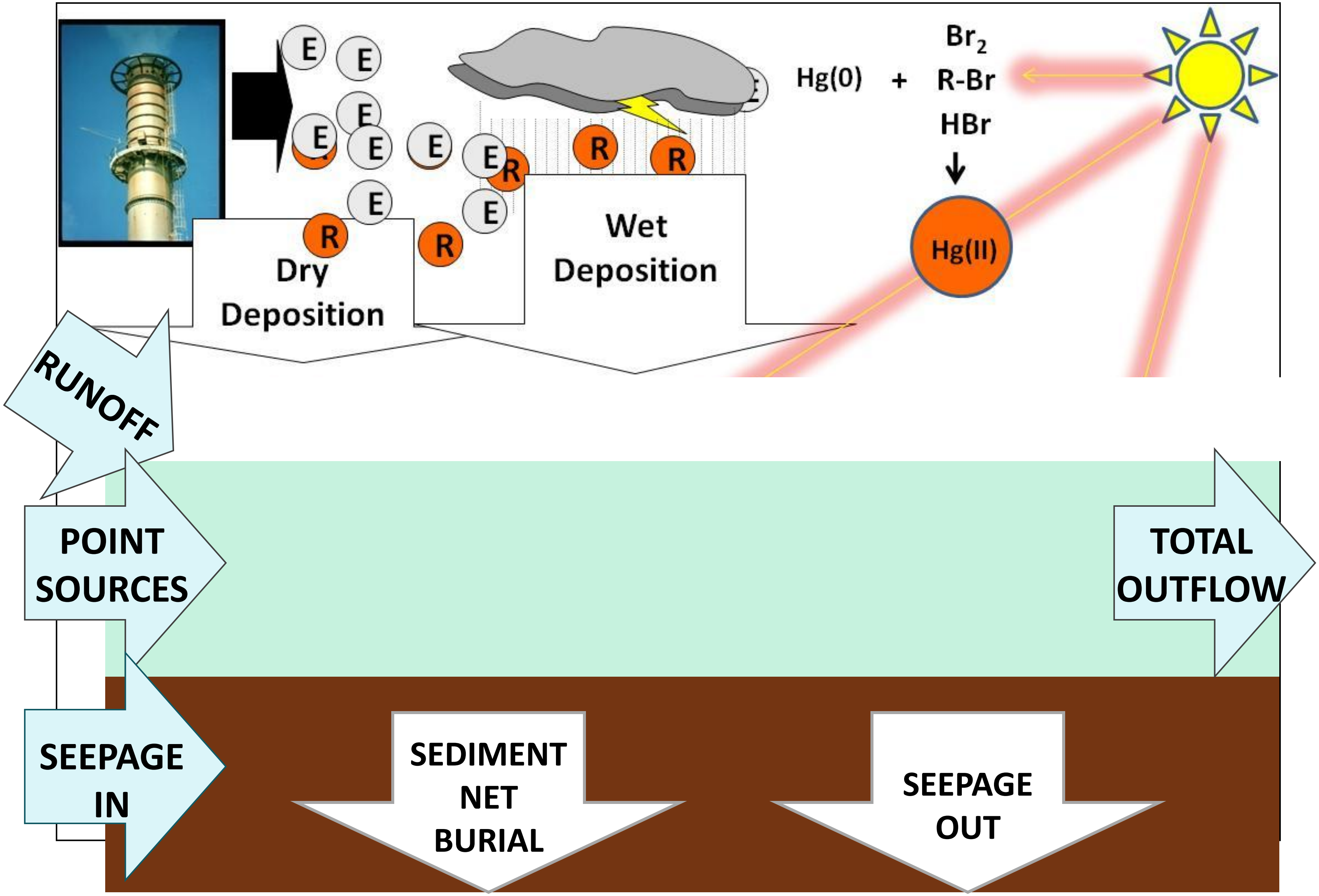
Summary of the Mercury Problem in the USA

Source: USEPA, 2008

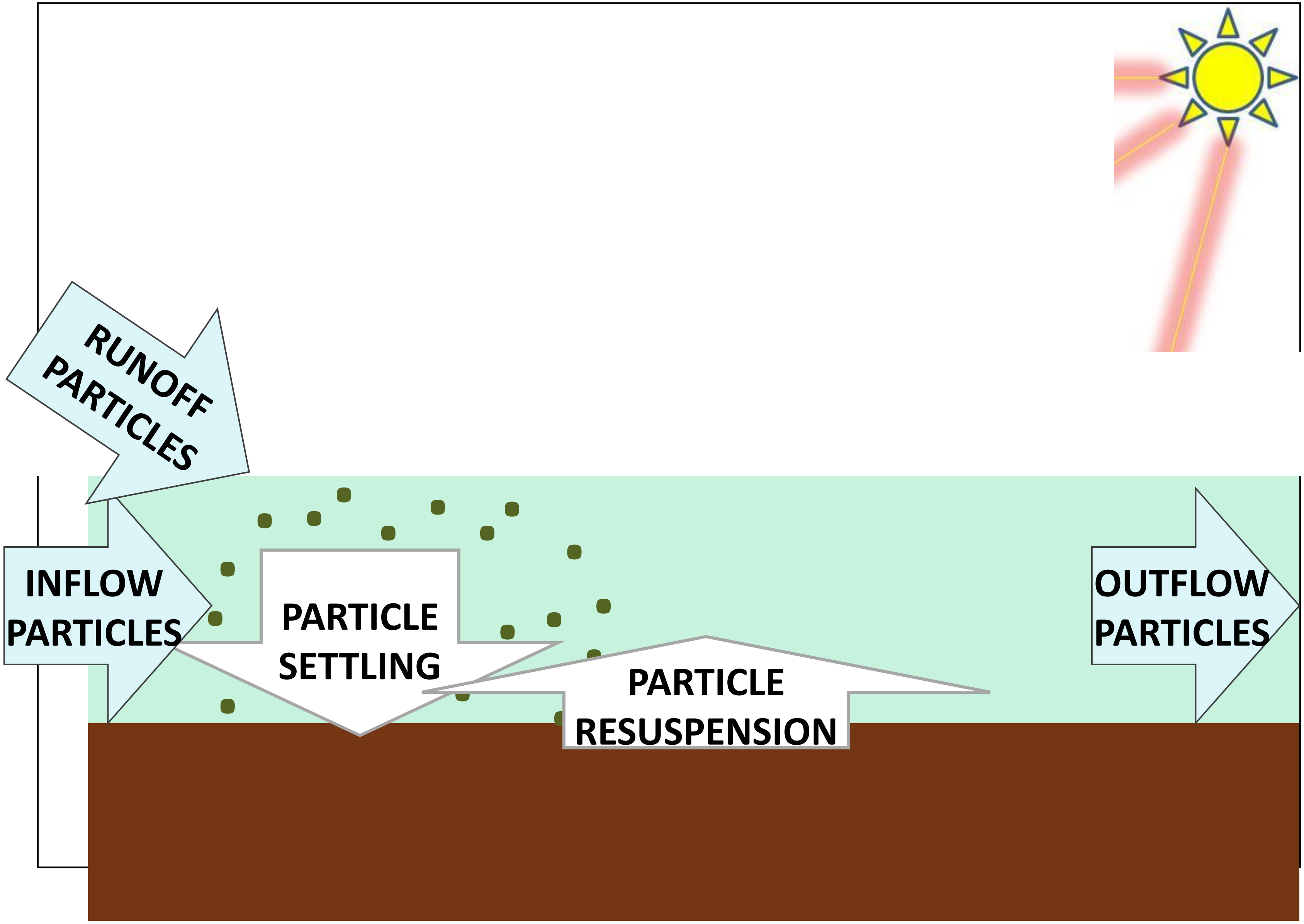
Mercury Conceptual Model

- Sources
- Transport
- Exchange
- Storage
- Transformation
- Bioaccumulation
- Human and Terrestrial Wildlife Exposure
- Toxic Effects and Resource Impairment

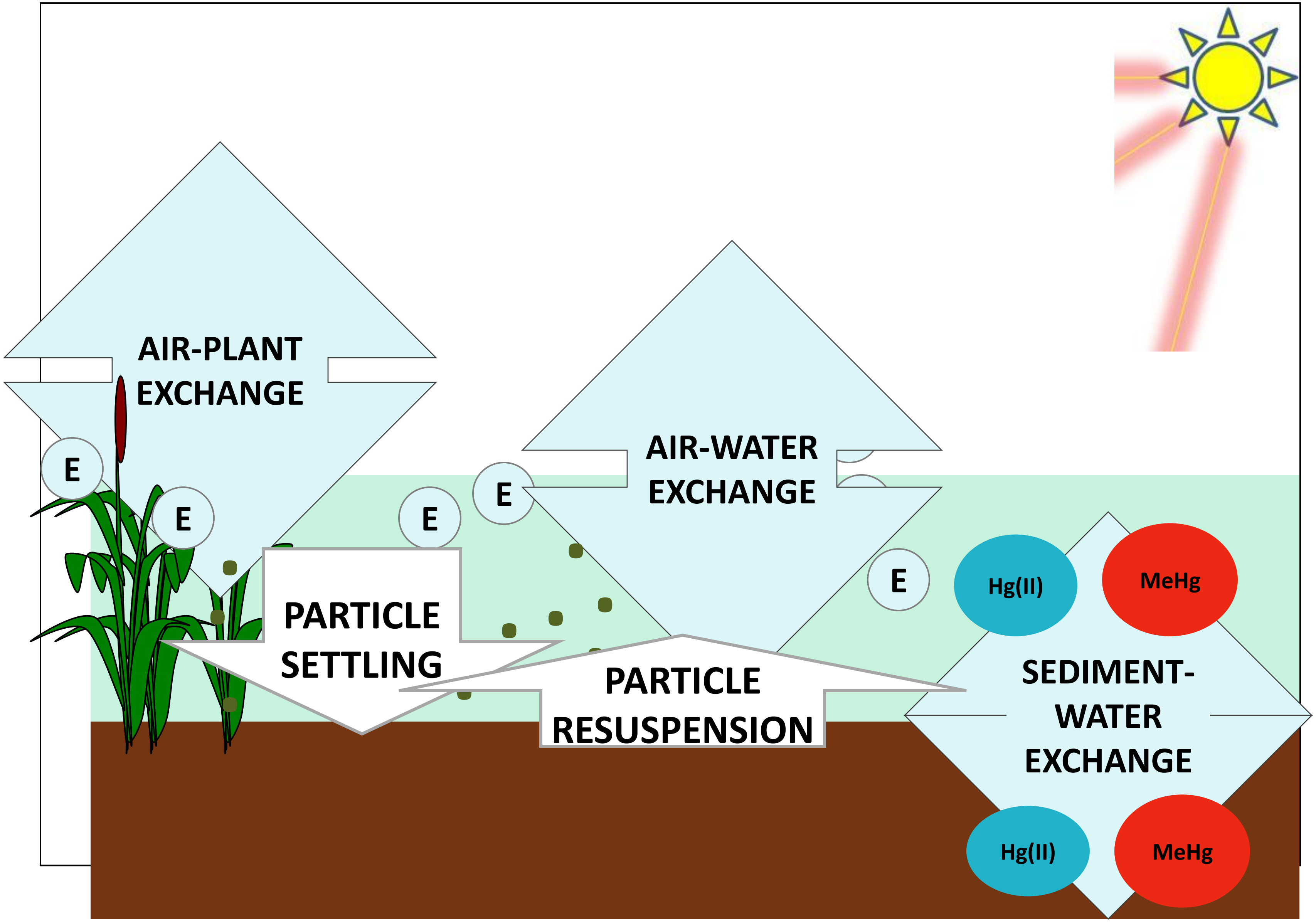
CONCEPTUAL MODEL OF WATER BODY Hg SOURCES



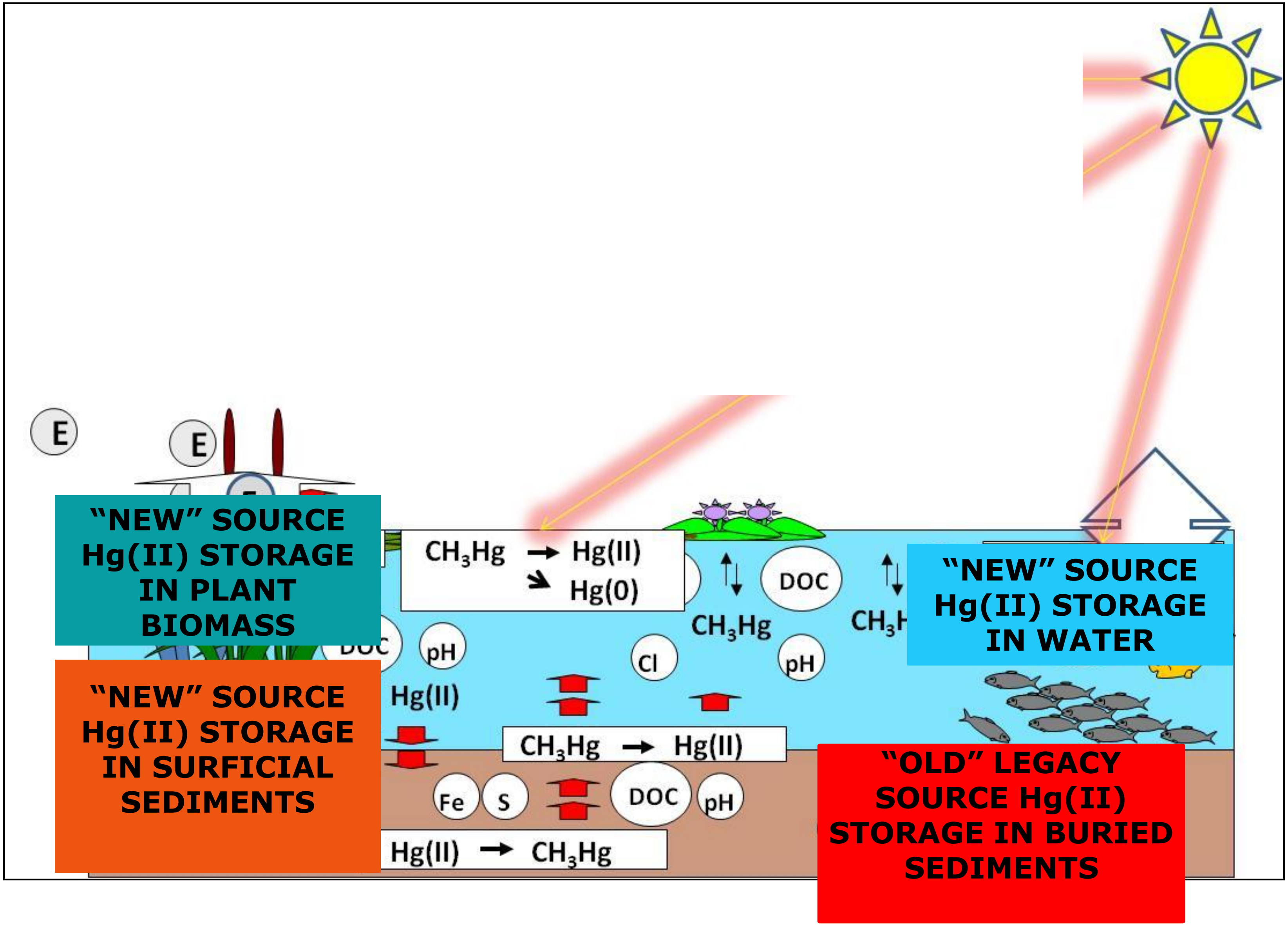
CONCEPTUAL MODEL OF WATER BODY Hg SOURCES



CONCEPTUAL MODEL OF Hg COMPARTMENT TRANSFERS



CONCEPTUAL MODEL OF Hg COMPARTMENT STORAGES



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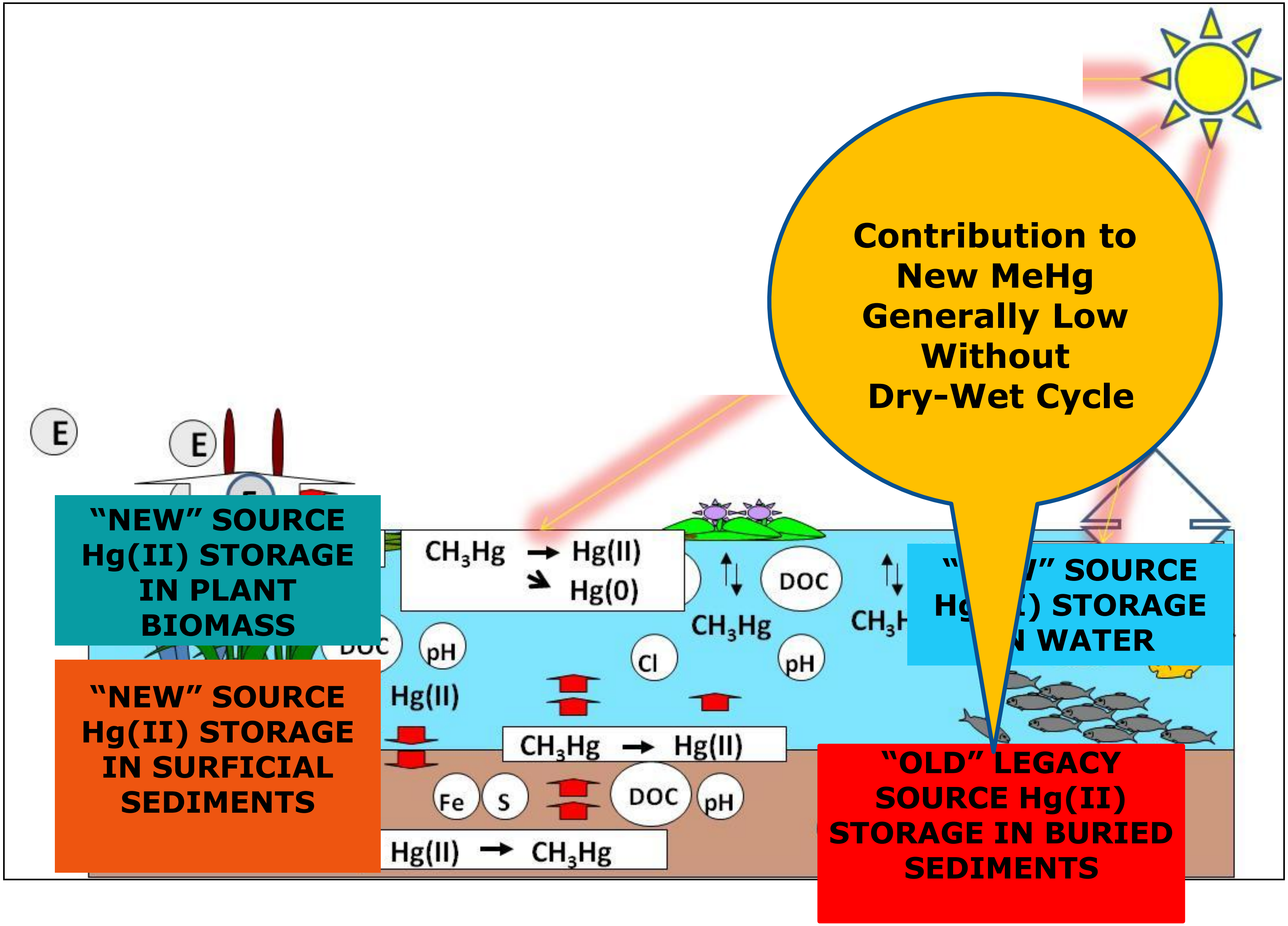
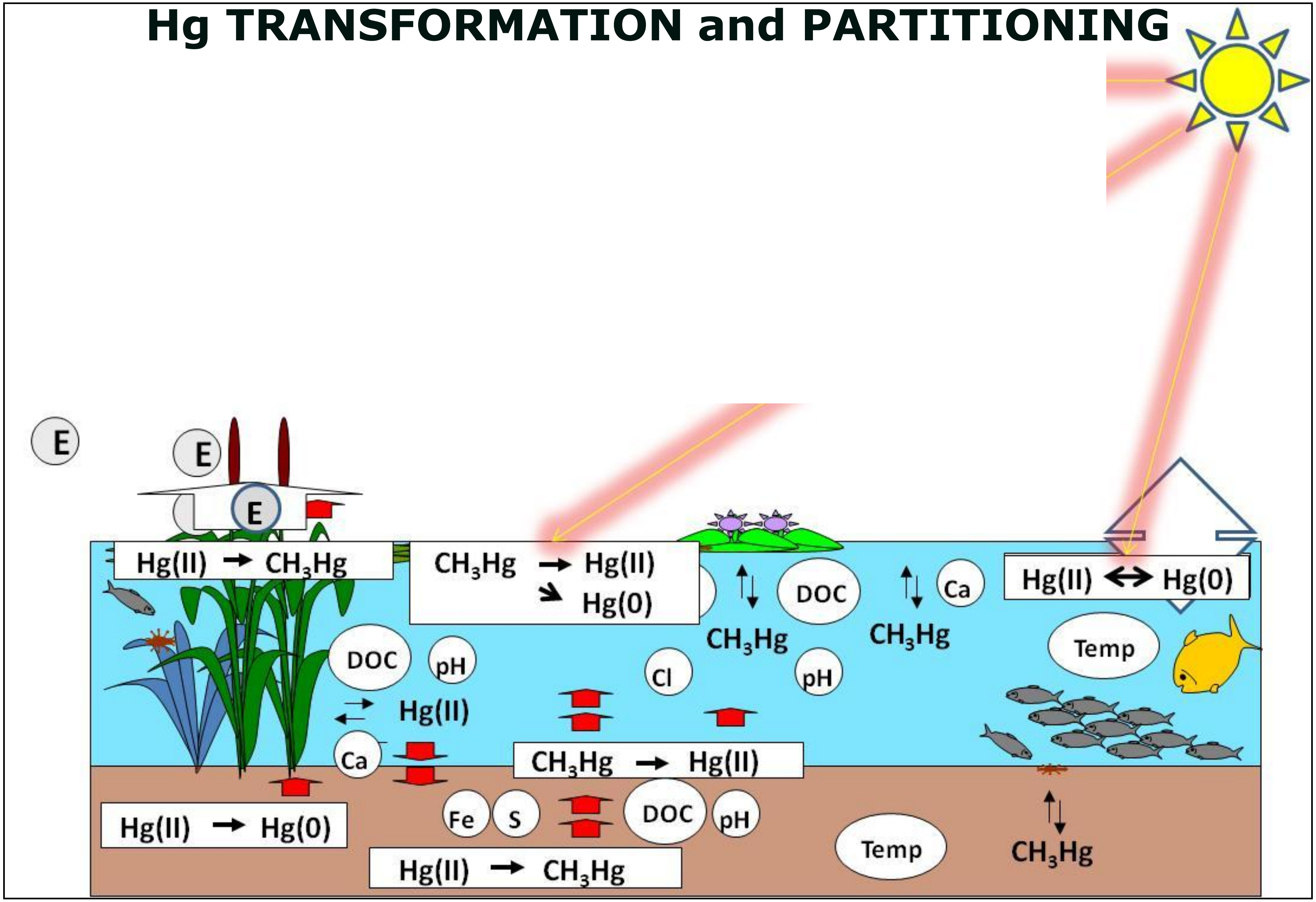
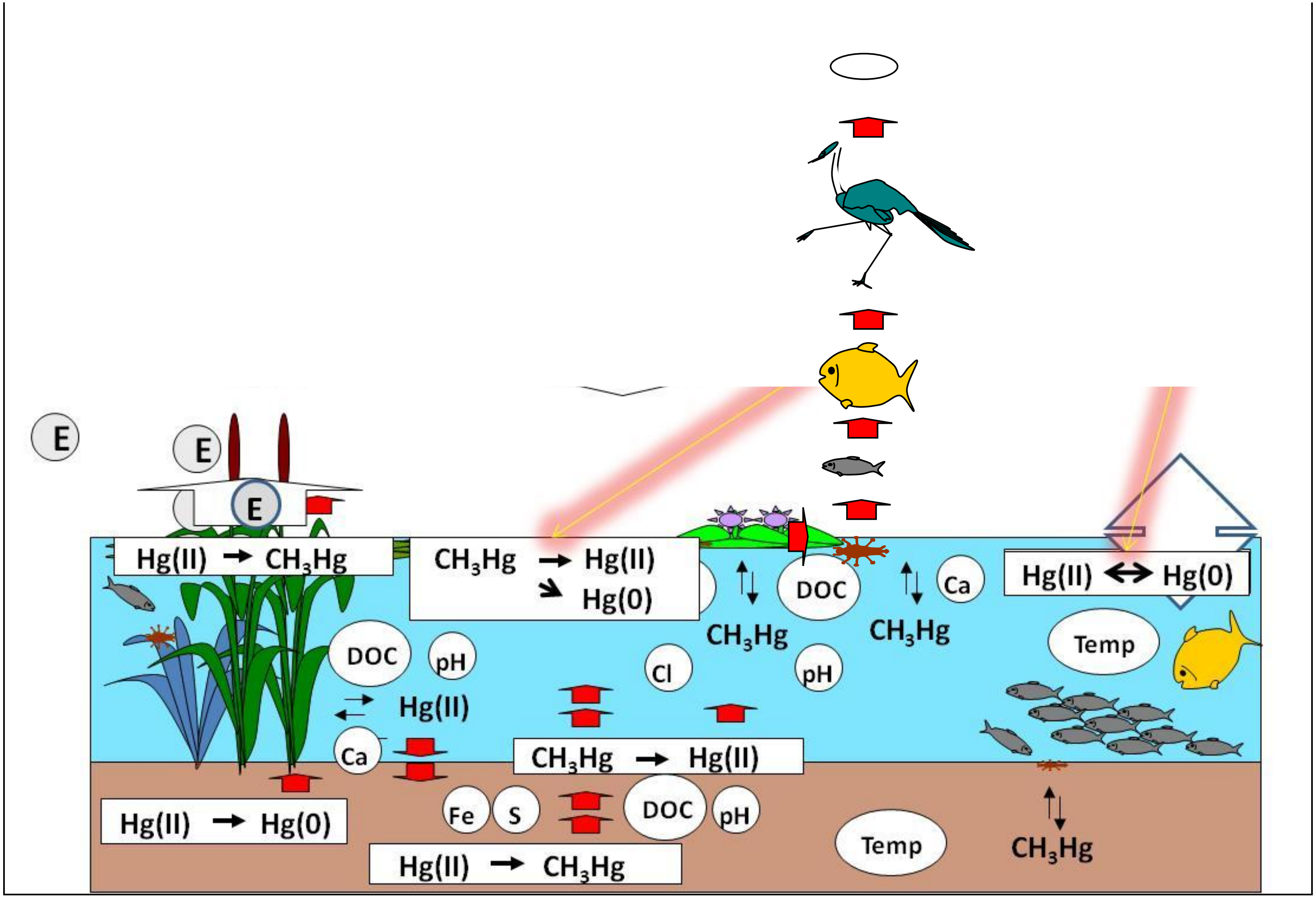


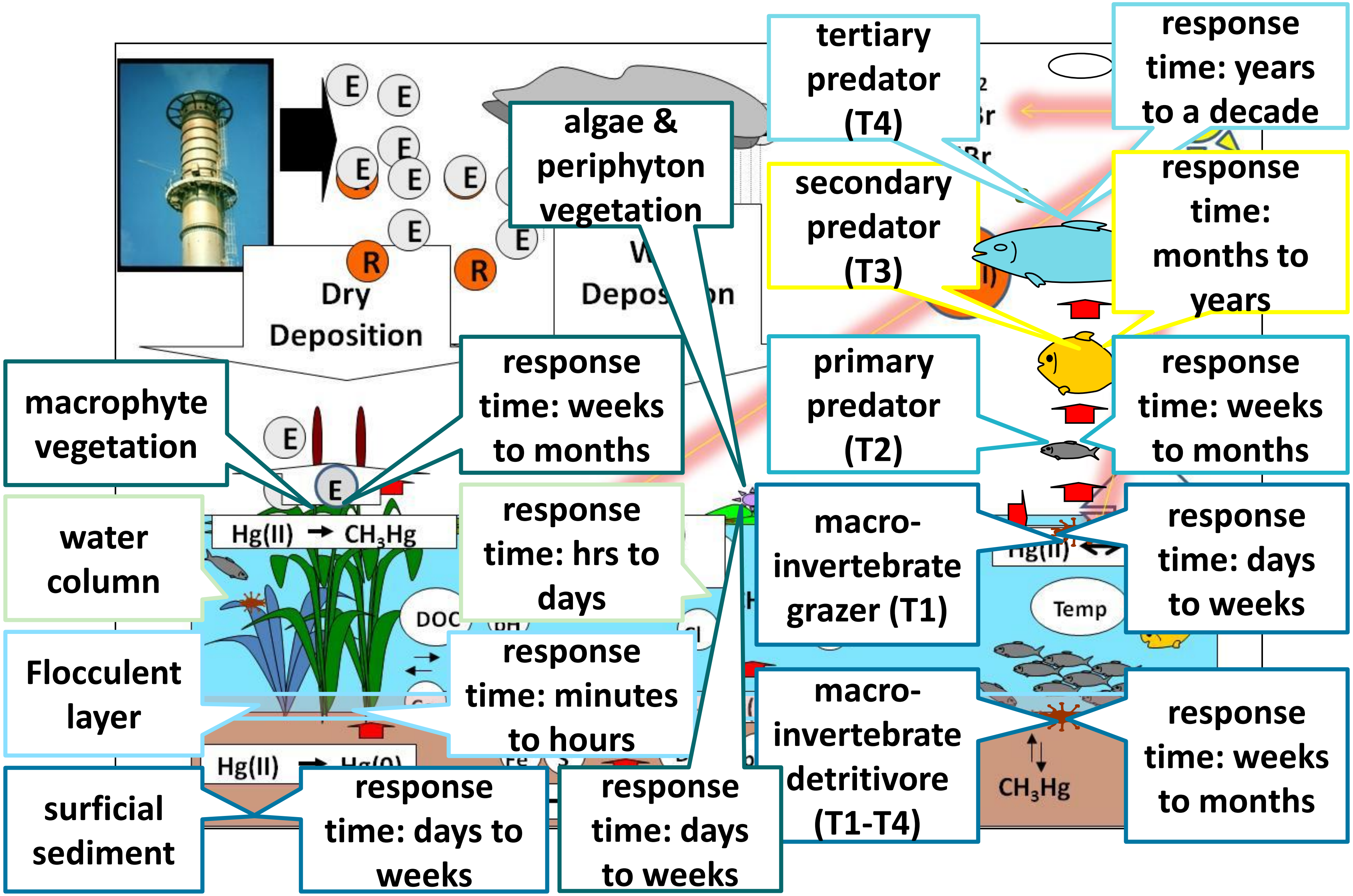
CONCEPTUAL MODEL OF
Hg TRANSFORMATION and PARTITIONING



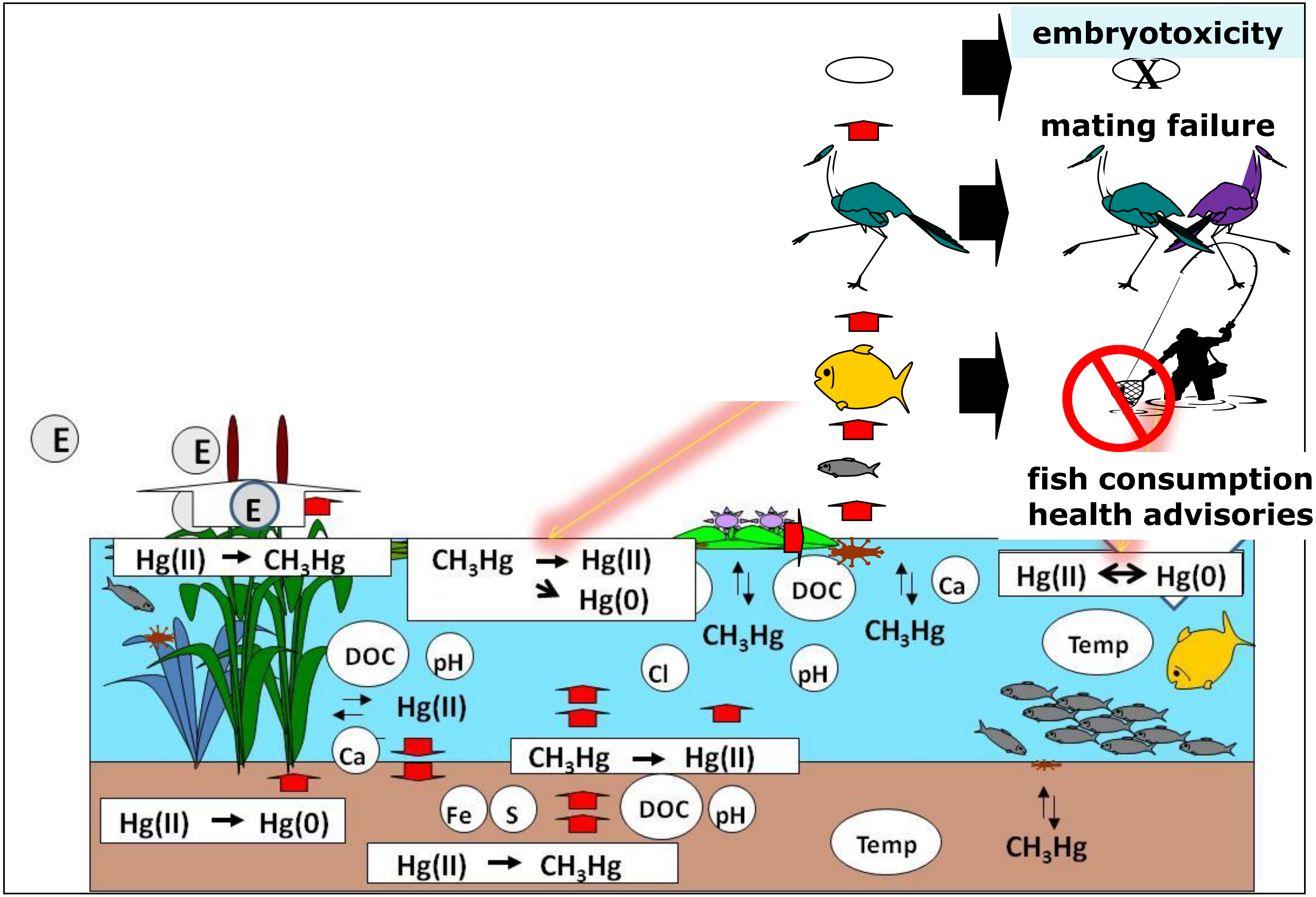
CONCEPTUAL MODEL of MeHg BIOMAGNIFICATION



CONCEPTUAL MODEL of MeHg Cycling Response Times



IMPAIRMENT OF RESOURCE USES, SERVICES and HABITATS



Characteristics of MeHg-Susceptible Watersheds and Water Bodies

Physical

- High Annual Rainfall
- High Watershed Surface Area-to-Lake Vol. Ratio
- High Surface-to-Subsurface Hydrology Ratio
- Frequent Floodplain Wet/Dry Cycle
- High Lake SA-to-V Ratio and Slow Flushing Rate (Long Hydraulic Residence Time)
- Low Runoff Sediment Loading Rate
- High Average Temperature and No Freeze-Over
- Stratification with Anoxic Hypolimnion
- Unconsolidated Sediments with High Diffusivity

Characteristics of MeHg-Susceptible Watersheds and Water Bodies

Chemical

- Low Limiting Nutrient Concentration
- Low Suspended Solids with Low Organic Carbon
- Low Water Column Dissolved Organic Carbon and Dissolved Inorganic Iron Filterable Colloid
- Low Alkalinity & Low pH
- Low DO at Sediment/Water Interface
- Unnatural Sulfate Loading > Background
- Low Sulfide in Zone of Maximum Net Methylation
- Optimum 0, C, S, Fe, Mn Ratios for Maximum Methylation and Minimum Demethylation Rates

Characteristics of a MeHg-Susceptible Watersheds and Water Bodies

Biological/Ecological

- High Upland Surface Area of Natural and Constructed Wetlands
- Low Primary Production
- Vertically Stratified Aerobic and Anaerobic Sediment Bacterial Communities
- High Densities & Rates of Sulfate-Reducing Bacteria (SRB) and Iron-Reducing Bacteria (IRB)
- Low Demethylating Bacteria Densities & Rates
- Long Autotrophic and Saprotrophic Food Chains
- Large, Slow-Growing Fish

THg Sources, Fate, MeHg Bioaccumulation & Resource Impairment