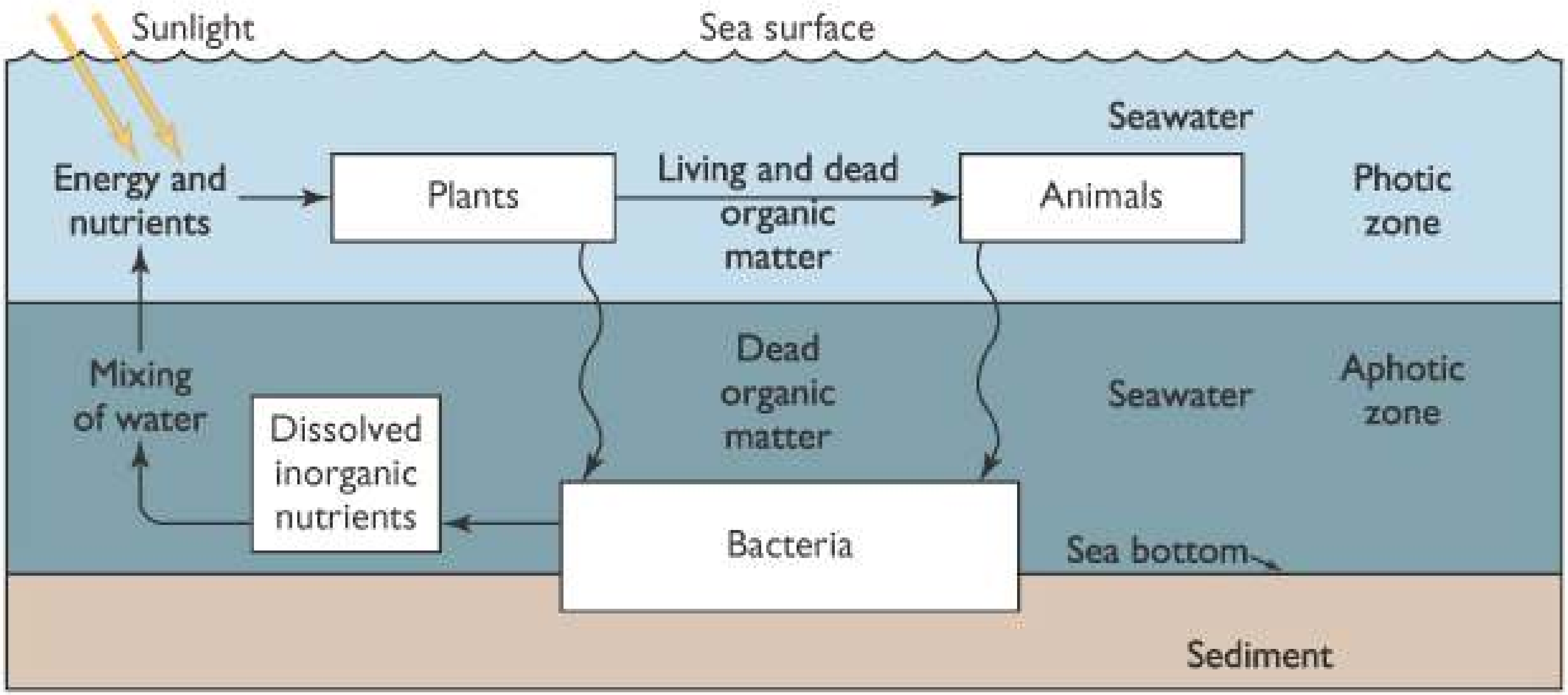
Siklus Biogeokimia di Perairan Pesisir dan Laut

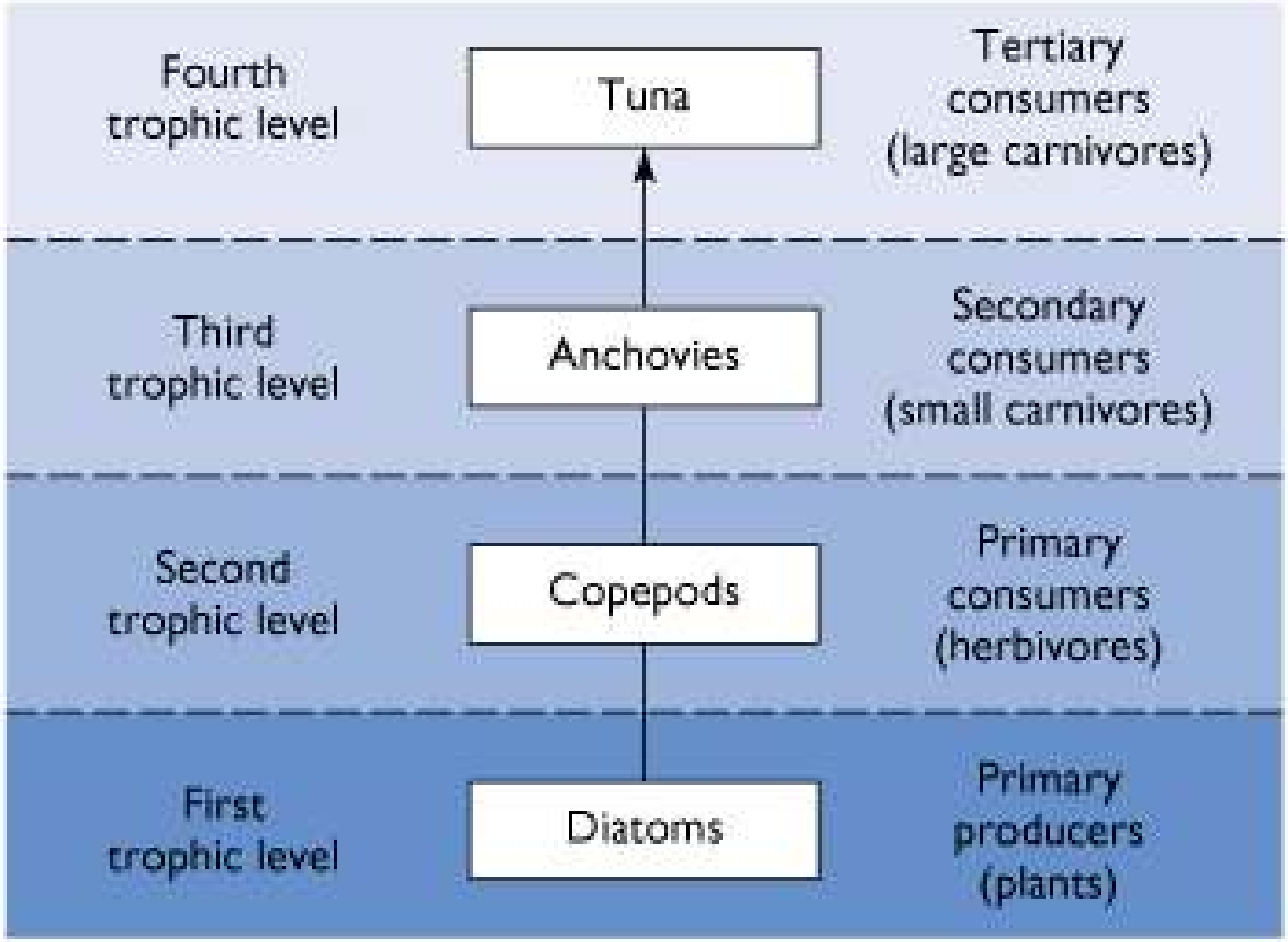
Siklus biogeokimia atau yang biasa disebut dengan siklus organik-anorganik adalah siklus unsur-unsur atau senyawa kimia yang mengalir dari komponen abiotik ke komponen biotik dan kembali lagi ke komponen abiotik. Siklus unsur-unsur tersebut tidak hanya melalui organisme, tetapi juga meli-batkan reaksi-reaksi kimia dalam lingkungan abiotik sehingga disebut sebgai siklus biogeokimia.

Diagram Ekosistem yang disederhanakan: SIKLUS NUTRIEN



(a) NUTRIENT CYCLING

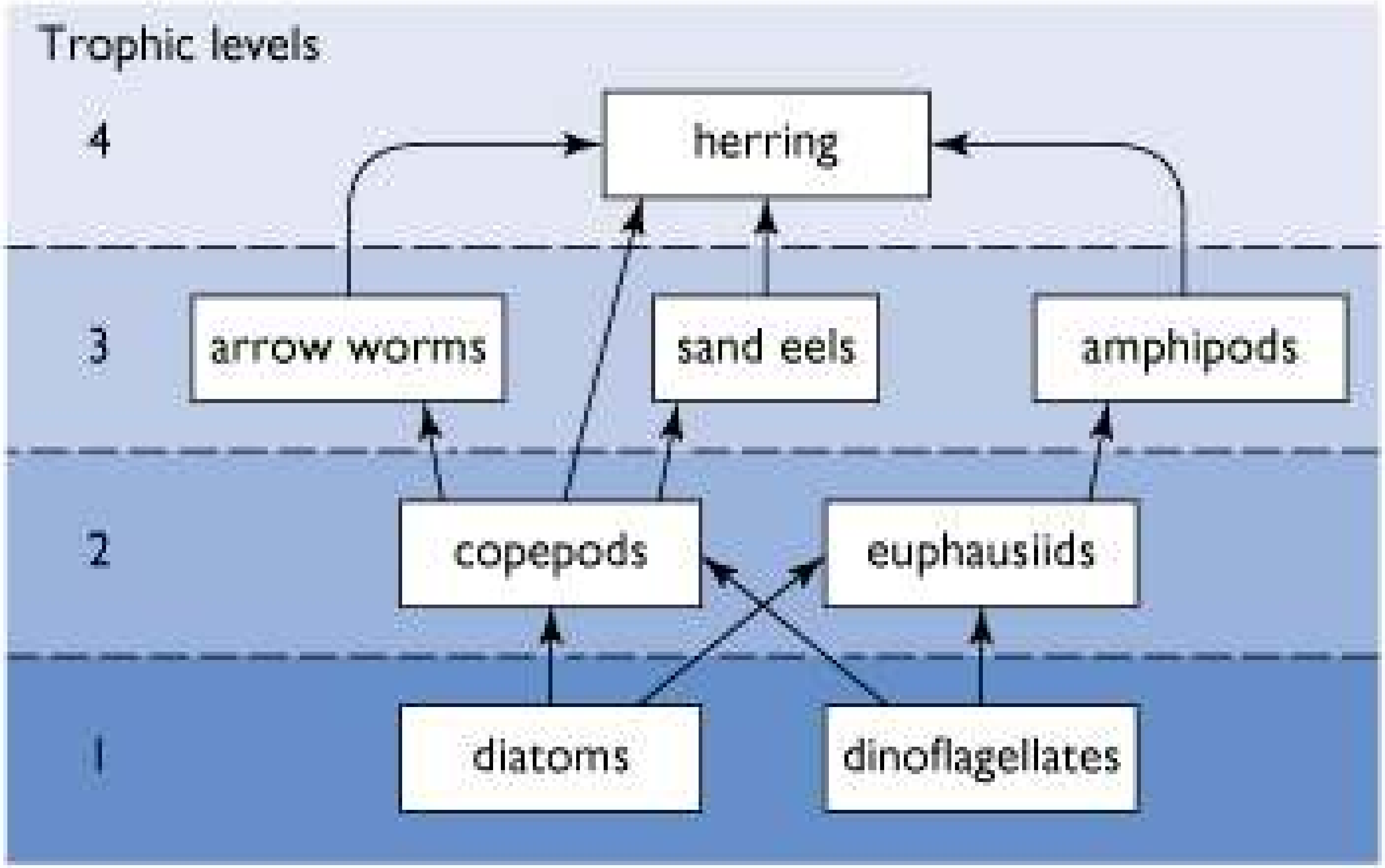
Struktur Ekosistem Lautan : Trofik level



(a) SIMPLE FOOD CHAIN

Struktur Ekosistem Lutan : Trofik level

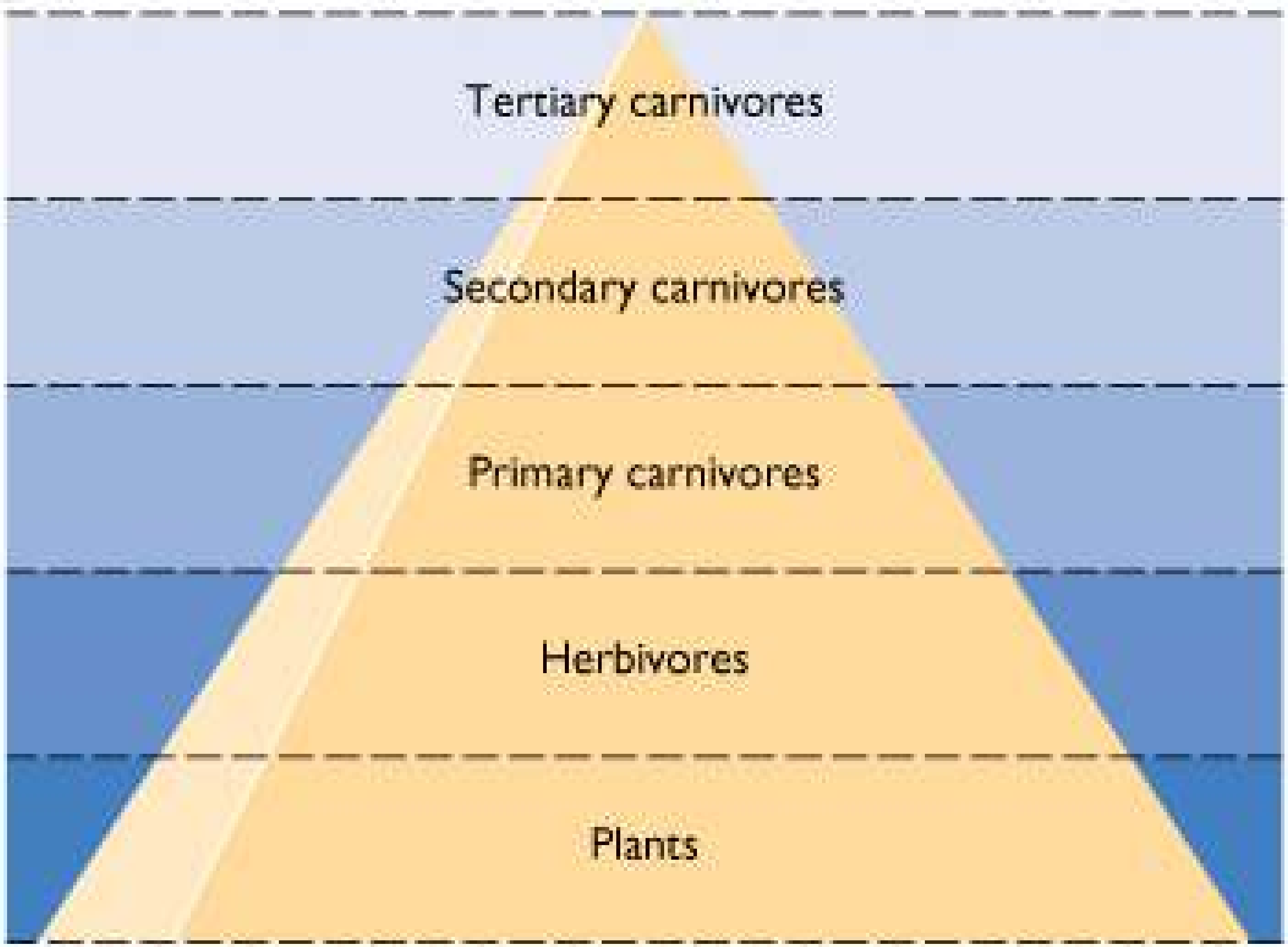
Contoh Food Web yg kompleks



(b) FOOD WEB

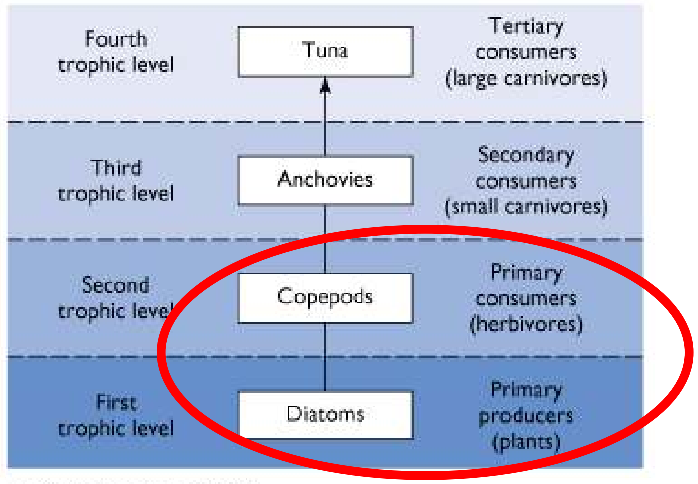
Struktur Ekosistem Lutan : Trofik level

Transfer Energi antar Trofik Level tidak efisien: PIRAMIDA ENERGI



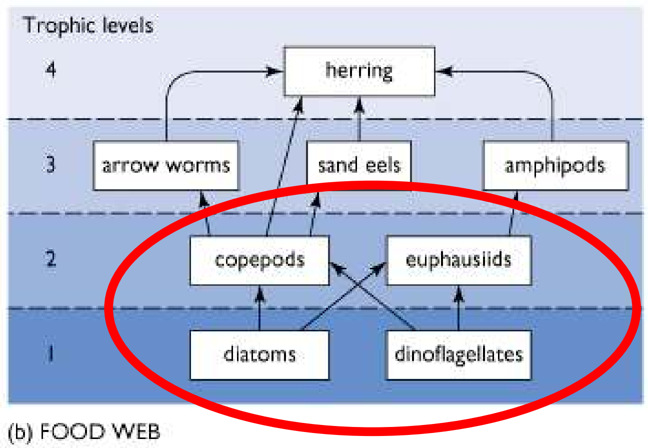
(c) ENERGY PYRAMID

Trofik level dan dinamikanya



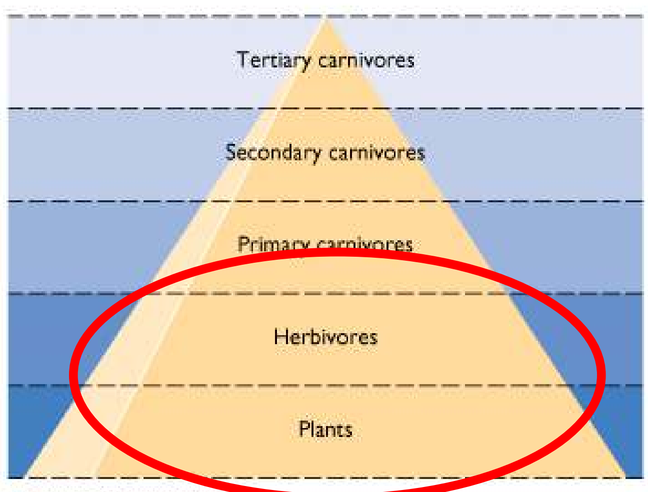
(a) SIMPLE FOOD CHAIN

Food Web



(b) FOOD WEB

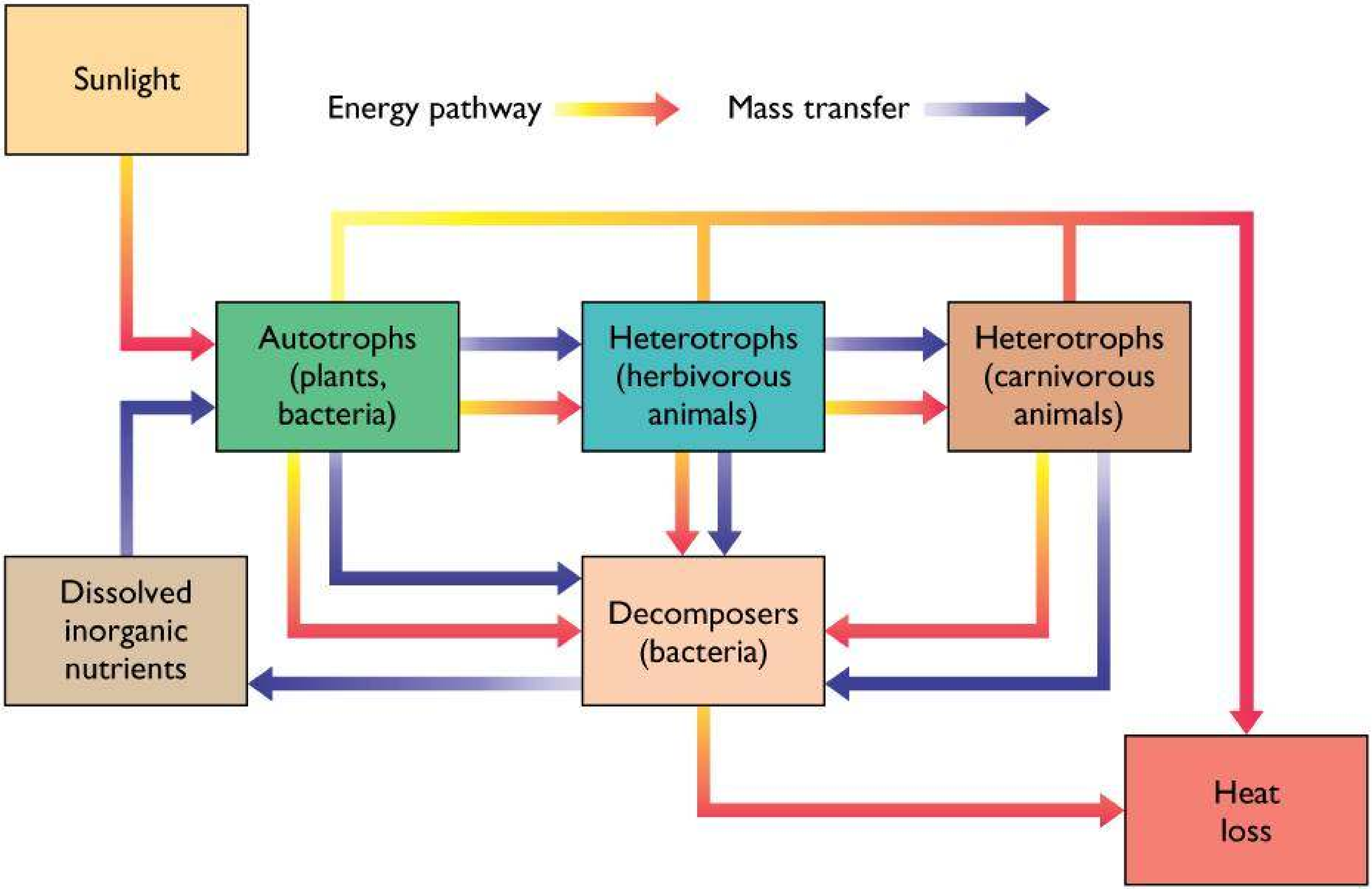
Piramida Energi



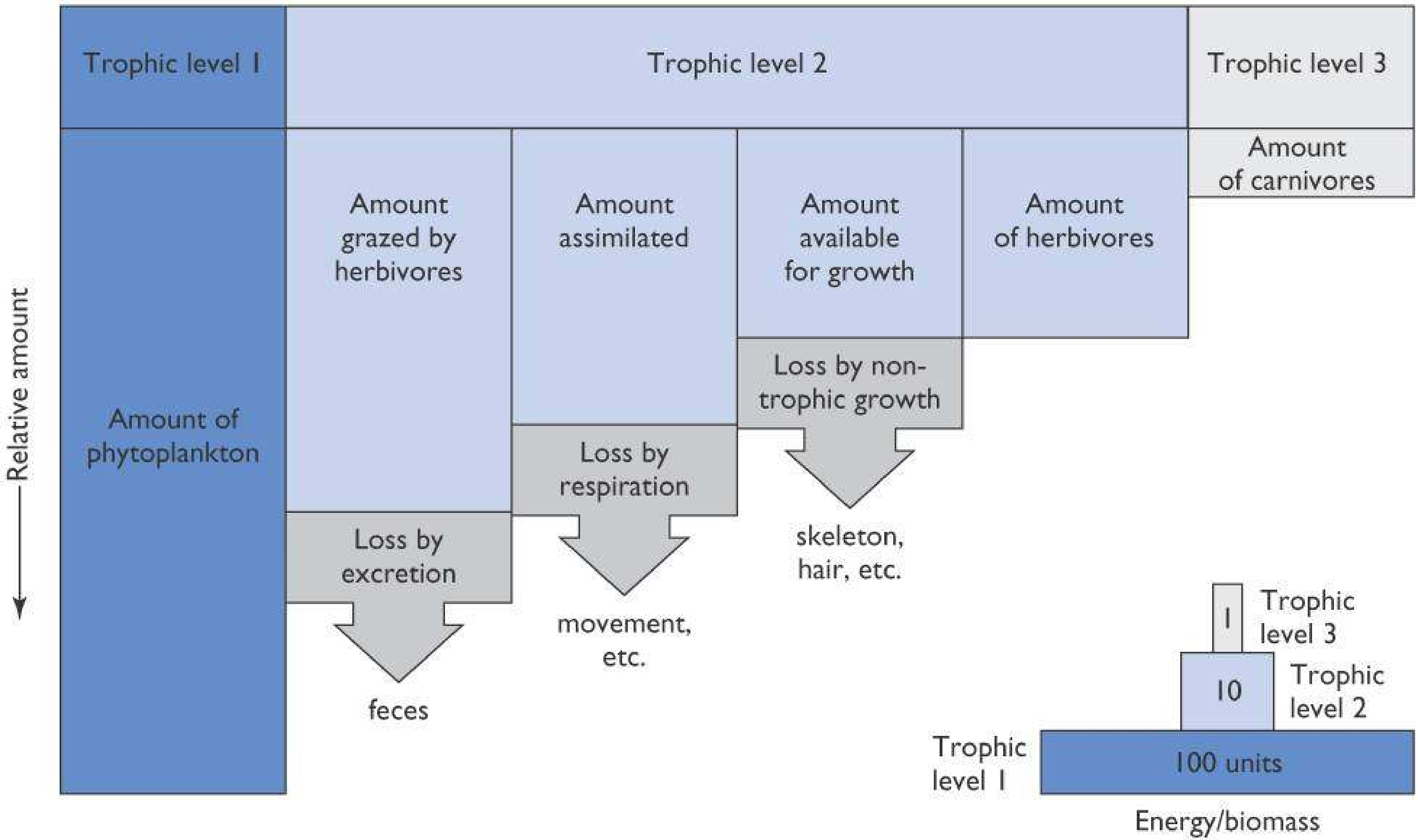
(c) ENERGY PYRAMID

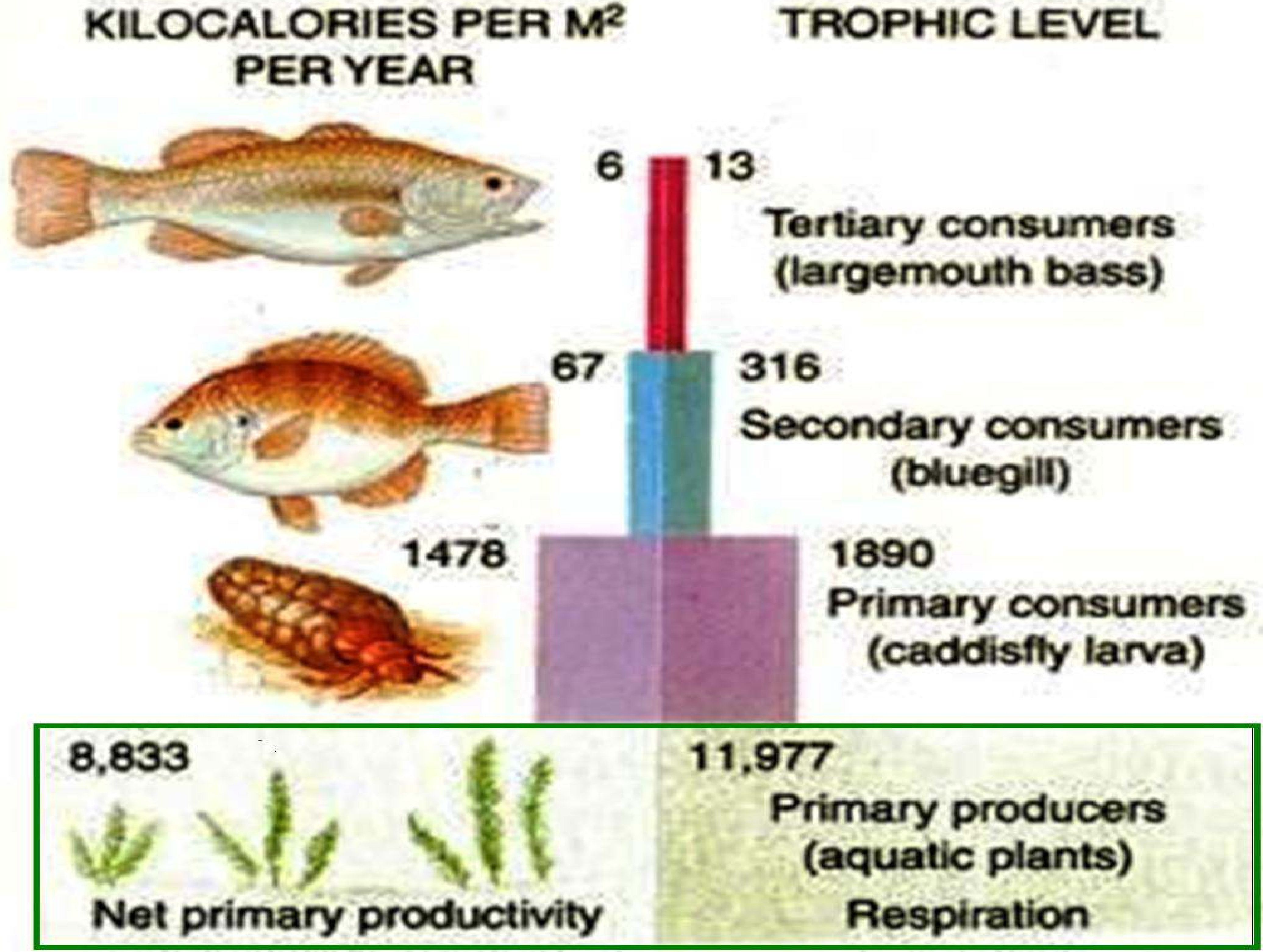
ENERGI

Ecosystem model.



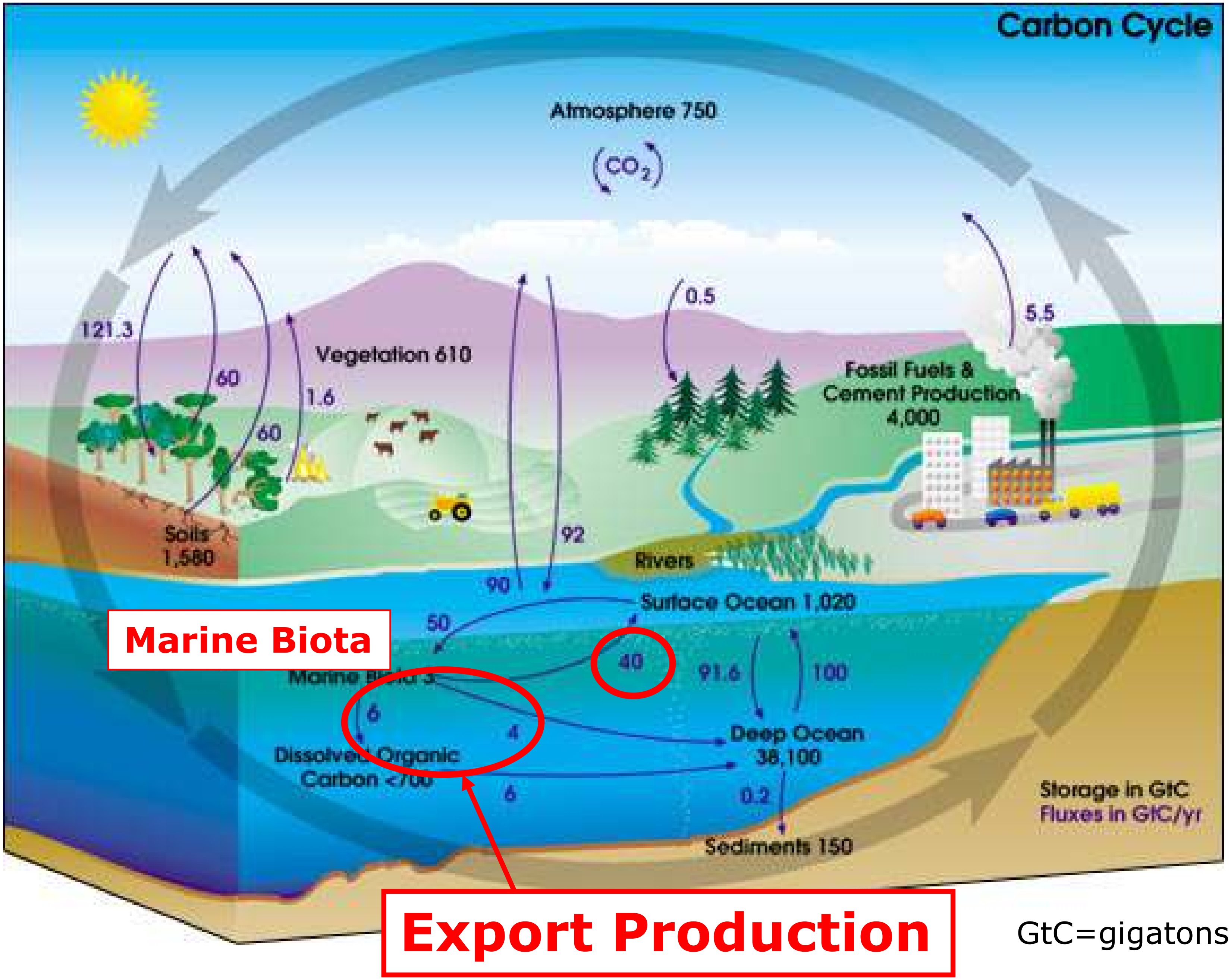
Energy transfer between trophic levels.





KILOCALORIES PER M² PER YEAR
TROPHIC LEVEL
6
13
Tertiary consumers (largemouth bass)
67
316
Secondary consumers (bluegill)
1478
1890
Primary consumers (caddisfly larva)
8,833
11,977
Primary producers (aquatic plants)
Net primary productivity
Respiration

Siklus Karbon



GtC=gigatons of carbon

Siklus Karbon di Laut: penyerapan CO_2 oleh tanaman utk fotosintesa $\Rightarrow$ karbohidrat

CO_2 kembali ke laut:

- **primer: respirasi tanaman, hewan dan bakteria**
- **sekunder: dekomposisi autolytic (oleh aksi enzym pada sel tissu organik dan tidak perlu bakteri)**

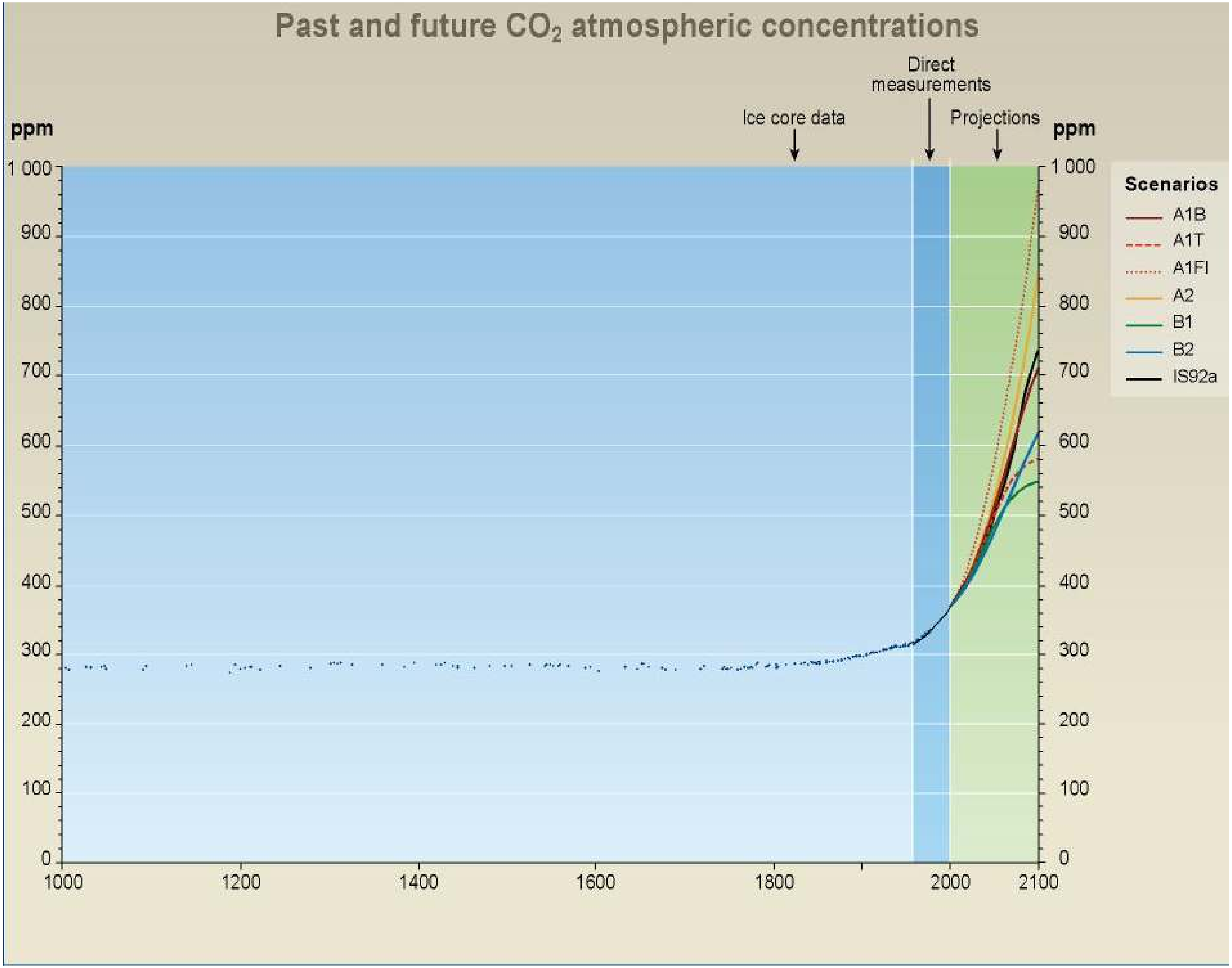
Bentuk CO_2 di laut:

- **bentuk molekul gas CO_2**
- **asam karbonat H_2CO_3**
- **ion bikarbonat HCO_3^-**
- **ion karbonat CO_3^{--}**

Karbon Dioksida dan Sistem Karbonat

Kenapa penting?

1. Mengatur suhu planet bumi
2. Penting untuk kehidupan di laut
3. Mengatur pH massa air laut


Past and future CO2 atmospheric concentrations
Direct measurements
Ice core data
Projections
ppm
ppm
1 000
900
800
700
600
500
400
300
200
100
0
1000
1200
1400
1600
1800
2000
2100
Scenarios
A1B
A1T
A1FI
A2
B1
B2
IS92a

CO_2

Temperature

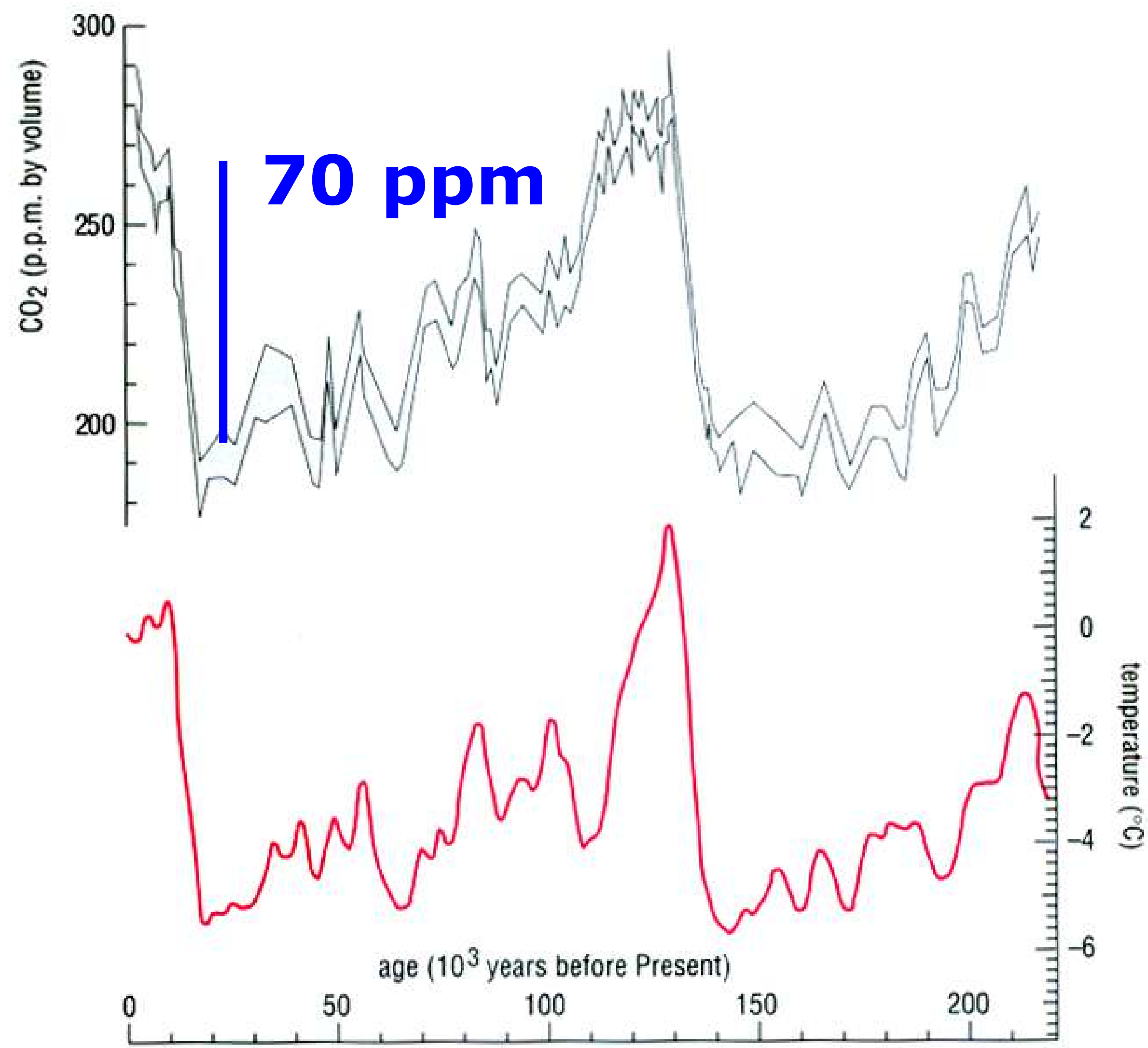
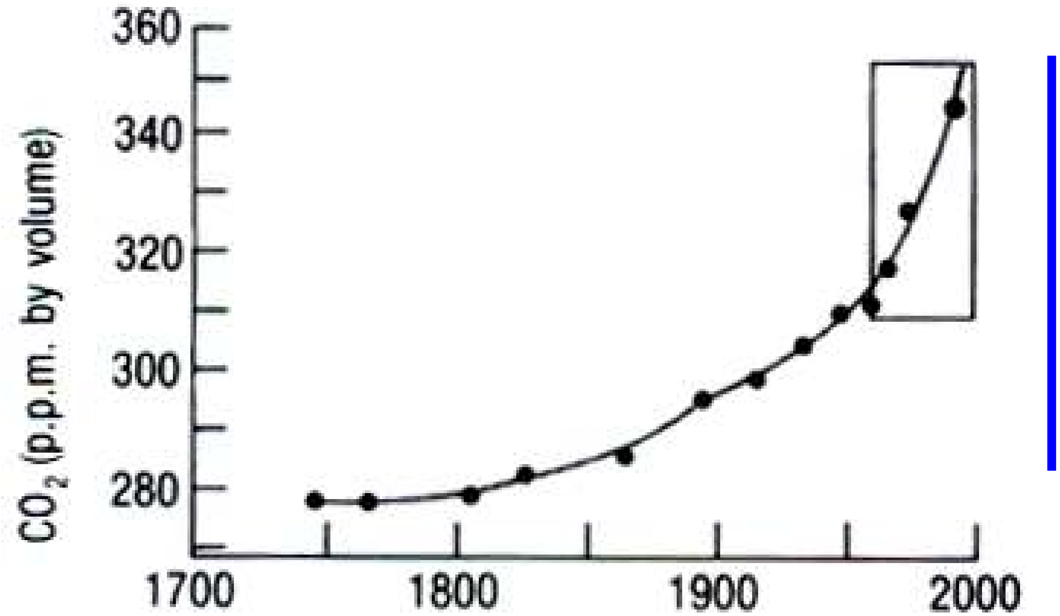


Figure 7.2 Variation with time in atmospheric CO_2 concentrations, determined from air bubbles trapped in an ice core from Vostok in eastern Antarctica (grey curve – width of shad area corresponds to measurement error); along with the atmospheric temperature at the surface, inferred from measurements of the deuterium/hydrogen isotopic ratio in H_2O (red curve).

Perubahan CO_2 pada 300 tahun terakhir



70 ppm

Revolusi Industri

Sistem Karbonat

Sumber karbon an-organik

Dari gas from CO_2 terlarut

$$H_2O + CO_2(gas) \rightleftarrows H_2CO_2(aq) \rightleftarrows$$

$$H^+ + HCO_3^-(aq) \rightleftarrows 2H^+ + CO_3^{2-}(aq)$$

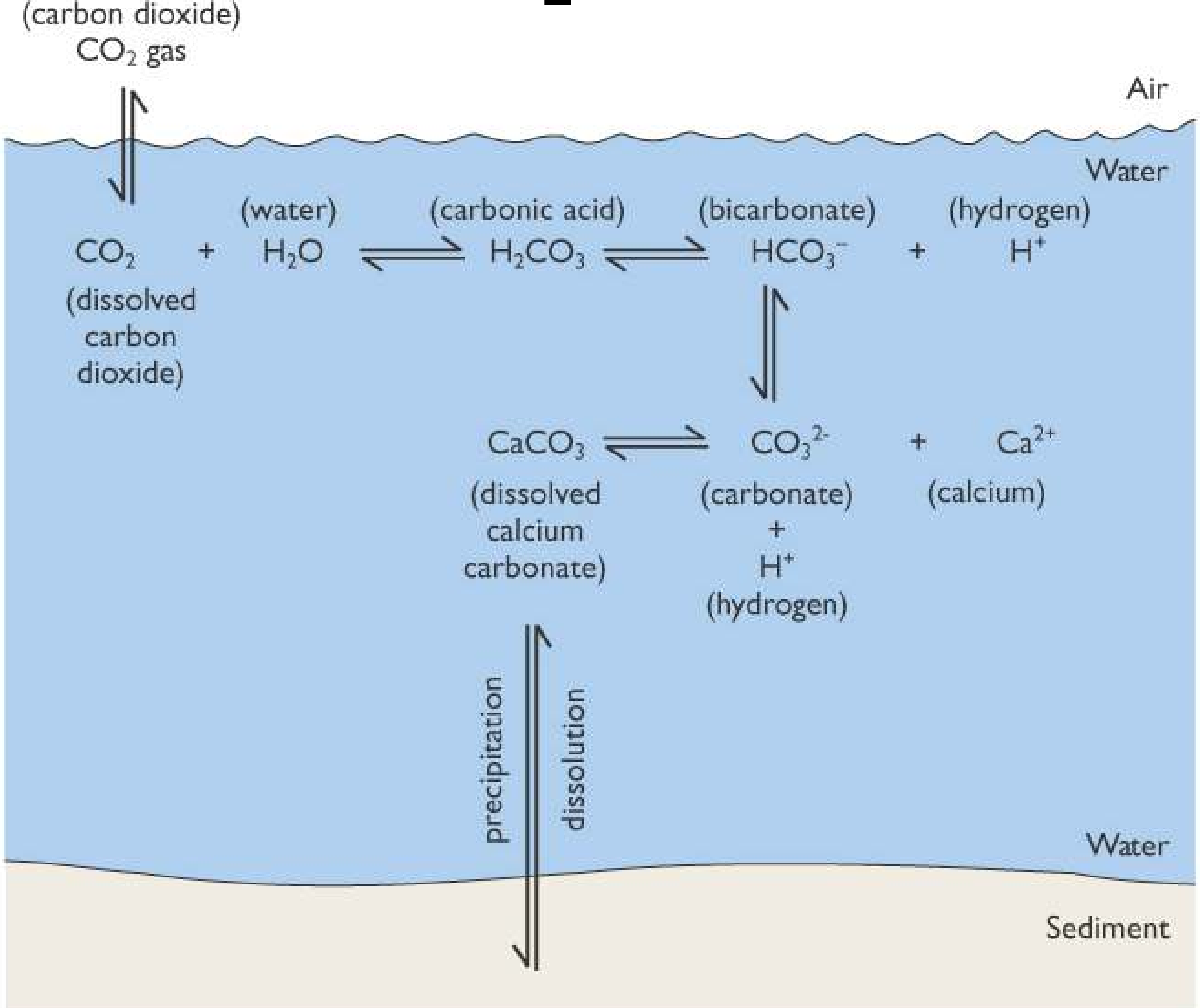
Dari disolusi (dissolution) Kalsium karbonat

$$CaCO_3(s) \rightleftarrows Ca^{2+}(aq) + CO_3^{2-}$$

NOTE:

Biology and Physics participate in the equilibrium of the carbonate system

CO_2 in the ocean



$$pH = -\log_{10}[H^+]$$

(c) THE CO_2 SYSTEM

Seawater too basic: $H_2CO_3 \longrightarrow HCO_3^- + H^+$ pH drops

Seawater too acidic: $HCO_3^- + H^+ \longrightarrow H_2CO_3$ pH rises

(d) CARBONATE BUFFER

Total an-organik karbon terlarut

Tidak ditemukan dalam bentuk ini

Ini sangat kecill

$$\sum CO_2 = CO_2(gas) + H_2CO_2(aq) + \\ + HCO_3^-(aq) + CO_3^{2-}(aq)$$

Total an-organik karbon terlarut:

$$\boxed{[\sum CO_2] = [HCO_3^-] + [CO_3^{2-}]}$$

Karbon Dioksida dan Sistem Karbonat

Asam karbonat

$$H_2O + CO_2(gas) \rightleftharpoons H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$$

$$HCO_3^- \rightleftharpoons 2H^+ + CO_3^{2-}$$

Ion Bikarbonat

Karbonat

Karbon Dioksida dan Sistem Karbonat

Menyebabkan pH lebih tinggi $\xleftarrow{\text{+ pH}}$

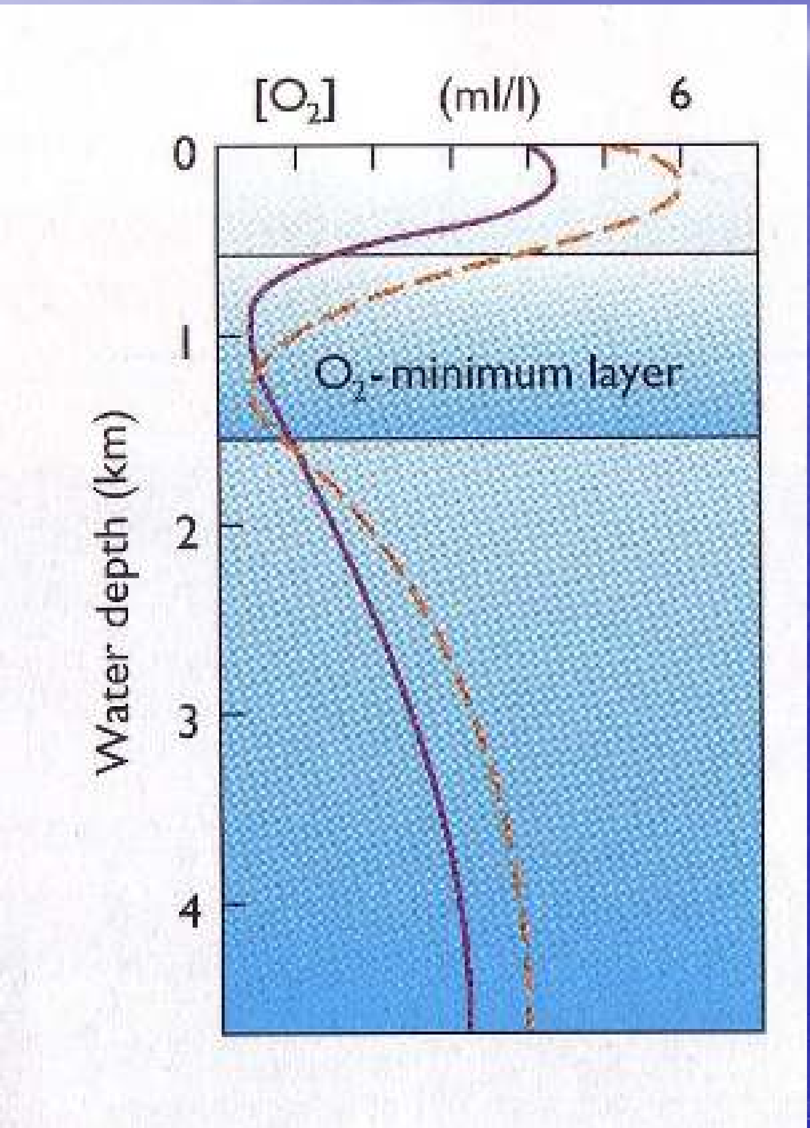
$$H_2O + CO_2(gas) \rightleftarrows H_2CO_3 \rightleftarrows H^+ + HCO_3^-$$

$$HCO_3^- \rightleftarrows 2H^+ + CO_3^{2-}$$

$\xrightarrow{\text{- pH}}$ **Menyebabkan pH lebih rendah**

Sistem buffer: pH sedikit alkalin: 8.1-8.3

Oksigen di perairan



Karakter oksigen dalam air:

1. Sebaran vertikal minimun di lapisan bawah,
2. Di permukaan kondisi supersaturasi

Faktor berpengaruh thd sebaran vertikal :

1. Kesetimbangan oksigen di lapisan udara dan permukaan air,
2. Proses fotosintesa di sub-permukaan,
3. Proses respirasi dan oksidasi,
4. Peningkatan oksigen dari sirkulasi air dasar

Faktor-faktor menentukan konsentrasi gas di air (O_2 dan CO_2)

Faktor	Pengaruhnya
Gelombang dan arus	Pertukaran gas air laut vs atmosfer meningkat
Perbedaan konsentrasi	Terjadi difusi gas antar muka air dan udara dari konsentrasi tinggi ke rendah hingga kondisi setimbang
Suhu	Suhu turun, daya larut menurun
Salinitas	Salinitas meningkat, daya larut turun
Tekanan	Tekanan meningkat, daya larut meningkat
Fotosintesa	Oksigen meningkat, CO_2 menurun
Respirasi	CO_2 meningkat, Oksigen menurun
Dekomposisi	CO_2 meningkat, Oksigen menurun
pH	Mengendalikan spesiasi CO_2 dalam air

SIKLUS NITROGEN

- Sumber nitrogen terbesar adalah udara. Udara mengandung 80% nitrogen
- Nitrogen lepas ke udara oleh kegiatan bakteri denitrifying
- Nitrogen masuk ke daur oleh kegiatan bakteri pengikat nitrogen atau algae dan melalui peristiwa elektrifikasi (halilintar)

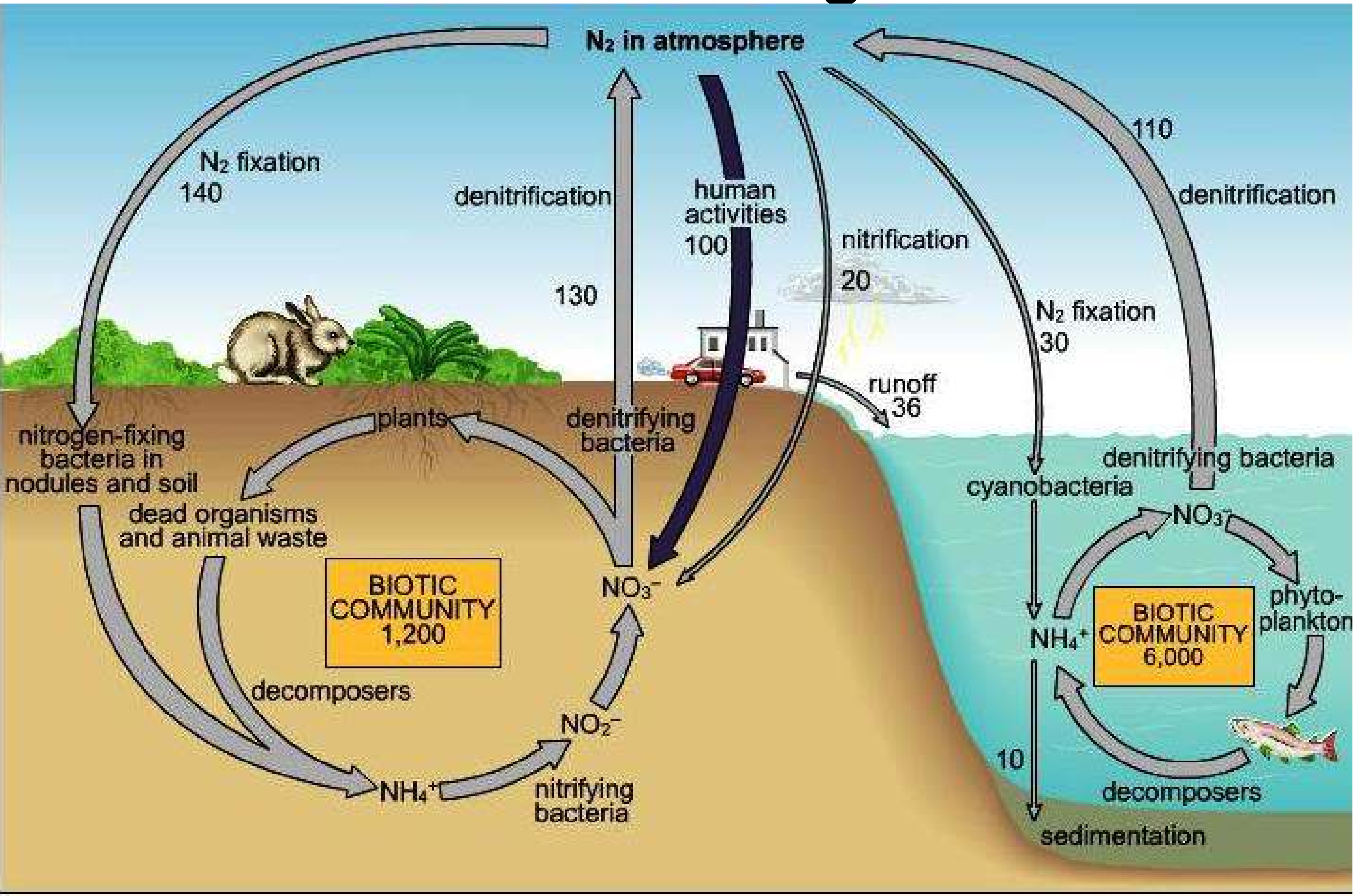
SIKLUS NITROGEN

- Nitrogen digunakan oleh tumbuhan dalam proses fotosintesis → utk produksi asam amino.
- Dimakan dan dicerna hewan dan diteruskan ke bakteria bersama dengan jaringan tumbuhan/hewan yang mati
- Bakteria mendapatkan energi dengan meme-cahkan ikatan tersebut dan melepaskan ikatan anorganik seperti nitrat yang merupa-kan unsur dasar hara yang digunakan tumbuhan

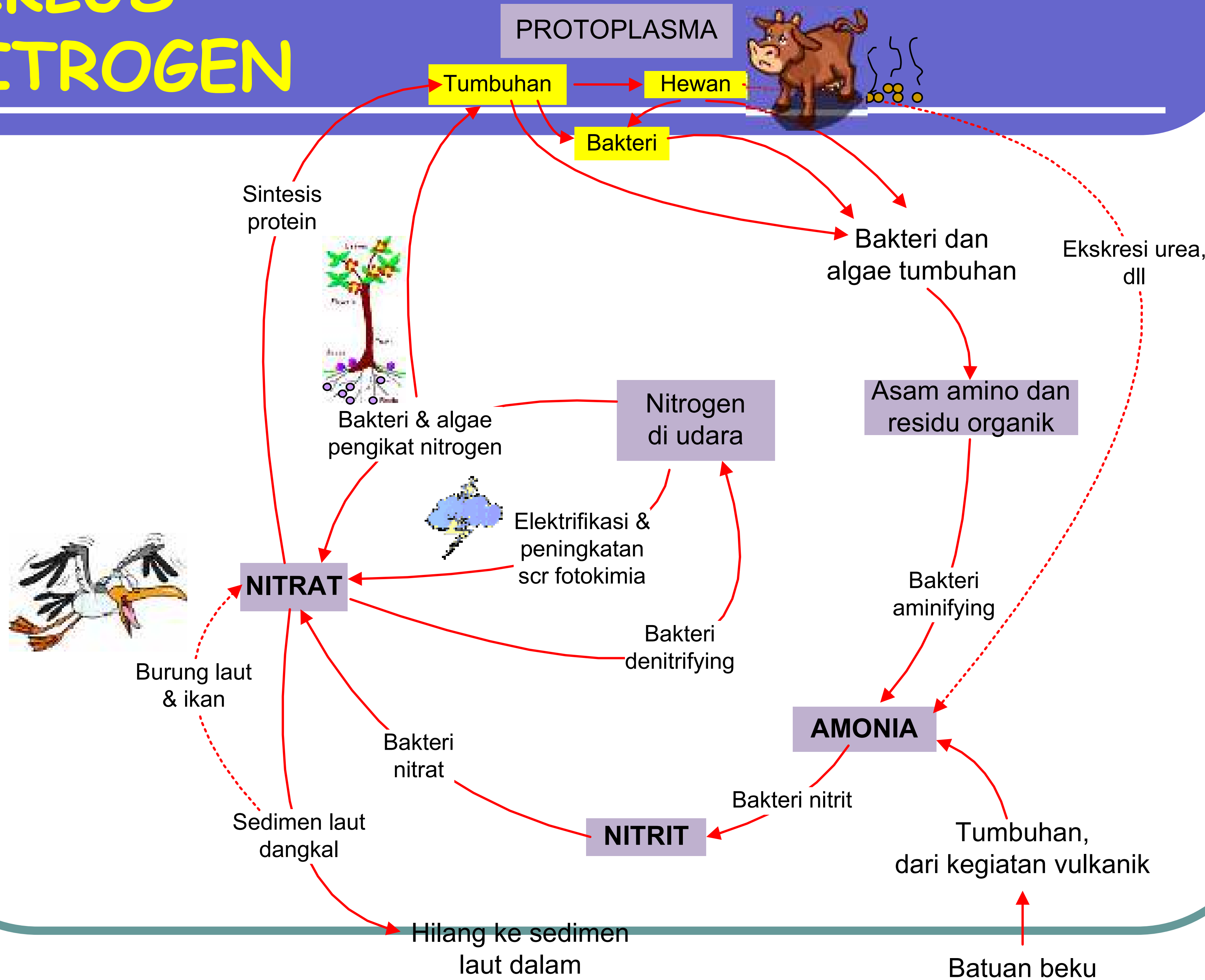
Organisme yg berperan dalam perubahan nitrogen :

- Bakteri nitrit: nitrosococcus dan nitrosomonas
- Bakteri nitrat: nitrobacter
- Bakteri aminifying: nitrosomonas
- Organisme pengikat nitrogen dari udara bebas:
  - Bakteri hidup bebas: Azotobacter dan Clostridium
  - Bakteri simbiotik: Rhizobium
  - Algae hijau biru: Anabaena, Nostoc

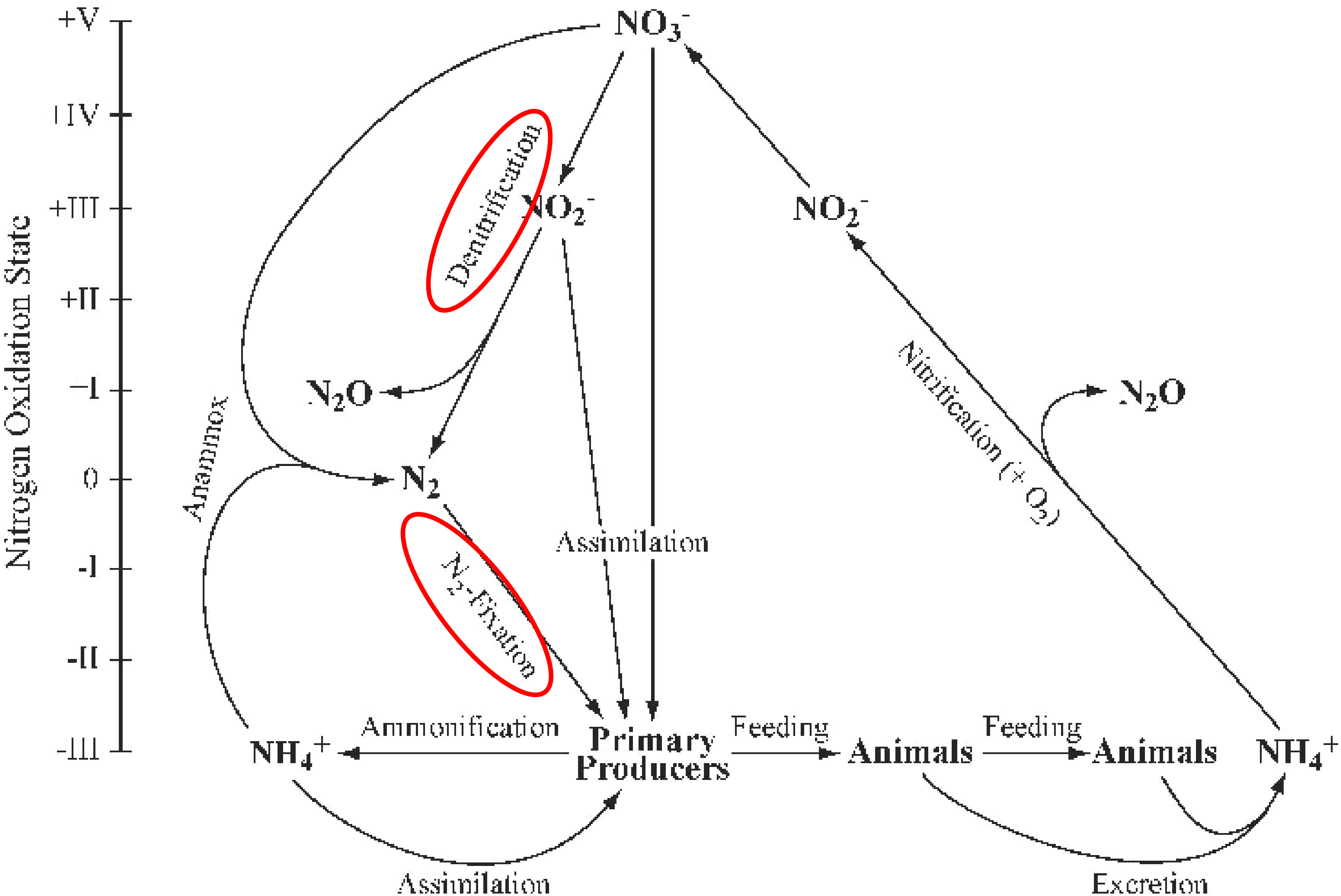
Siklus Nitrogen



SIKLUS NITROGEN



Transformsi Biologi Utama dari Nitrogen



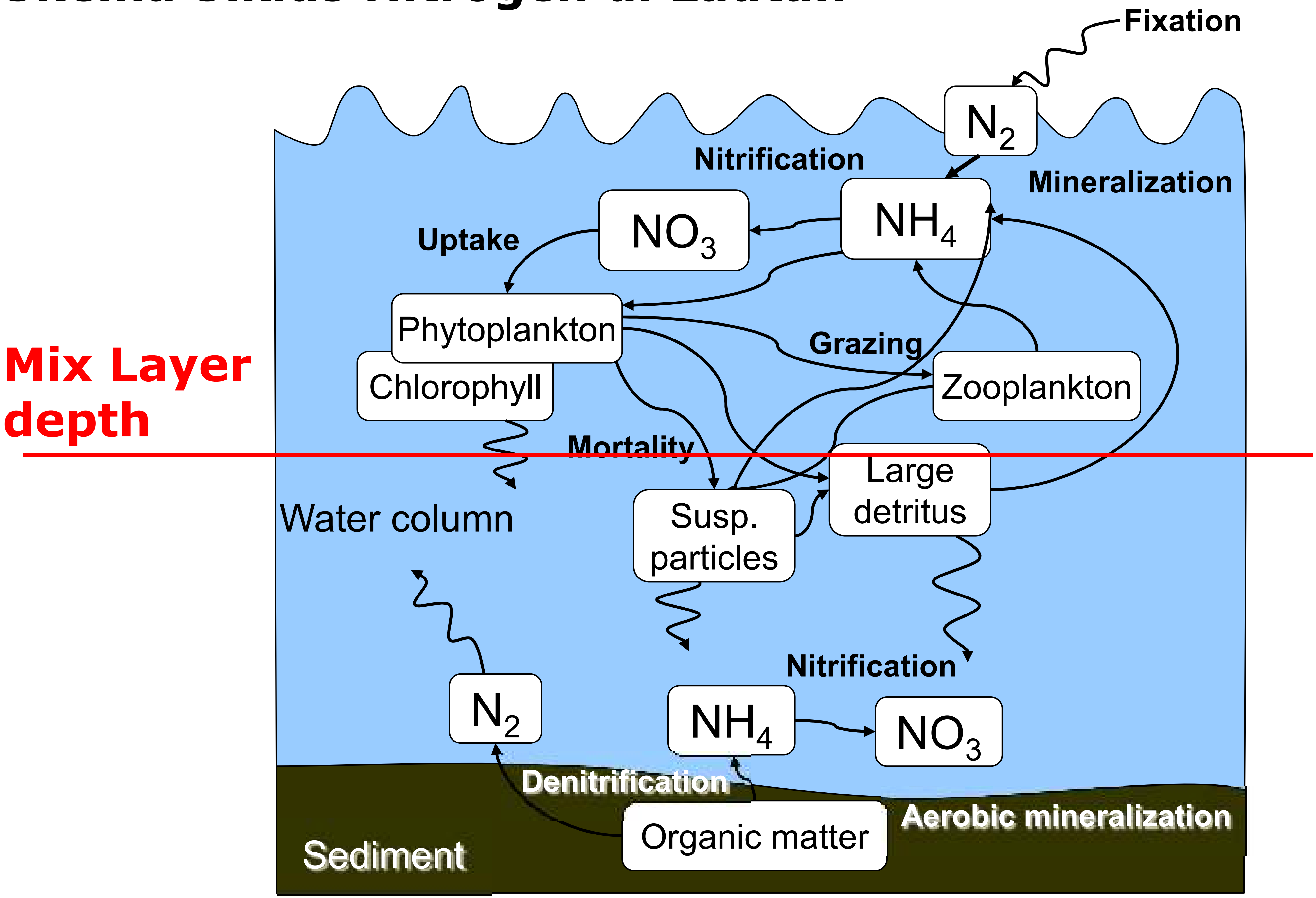
Bentuk nitrogen di lautan

- Nitrogen molekuler (gas) N_2
- Bentuk zat hara: Nitrit (NO_2) dan Nitrat (NO_3)
- Yang paling banyak: Ammonia (NH_4)

Ada berbagai bakteria yang terlibat dalam siklus Nitrogen $\Rightarrow$ agak rumit

Peran utama bakteri: konversi ikatan organik menjadi garam anorganik, ada juga yang dapat mengubah nitrogen molekular menjadi ikatan nitrogen (nitrogen-fixing bacteria)

Skema Siklus Nitrogen di Lautan



Siklus Nitrogen

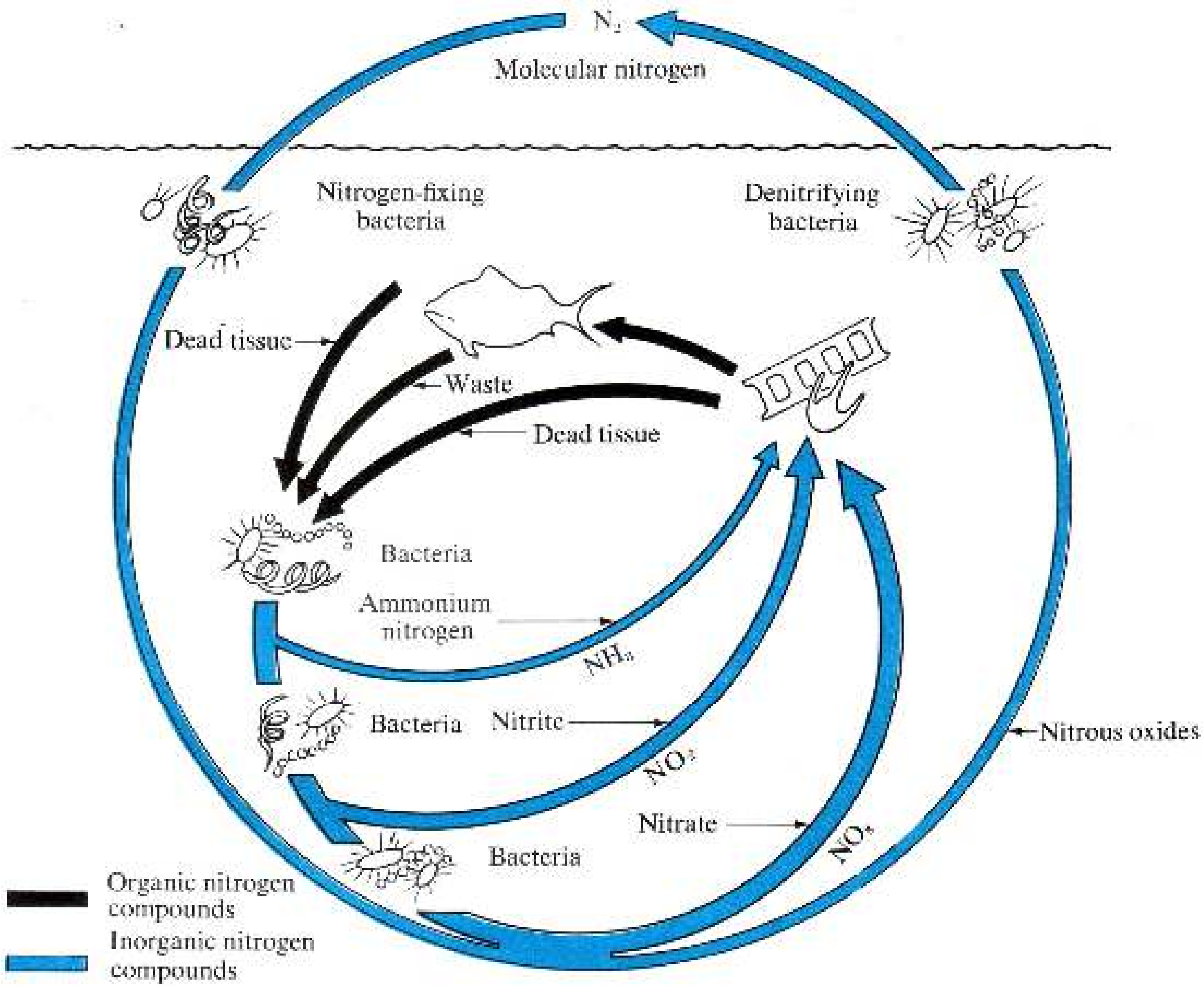


Figure 15–13 Nitrogen Cycle

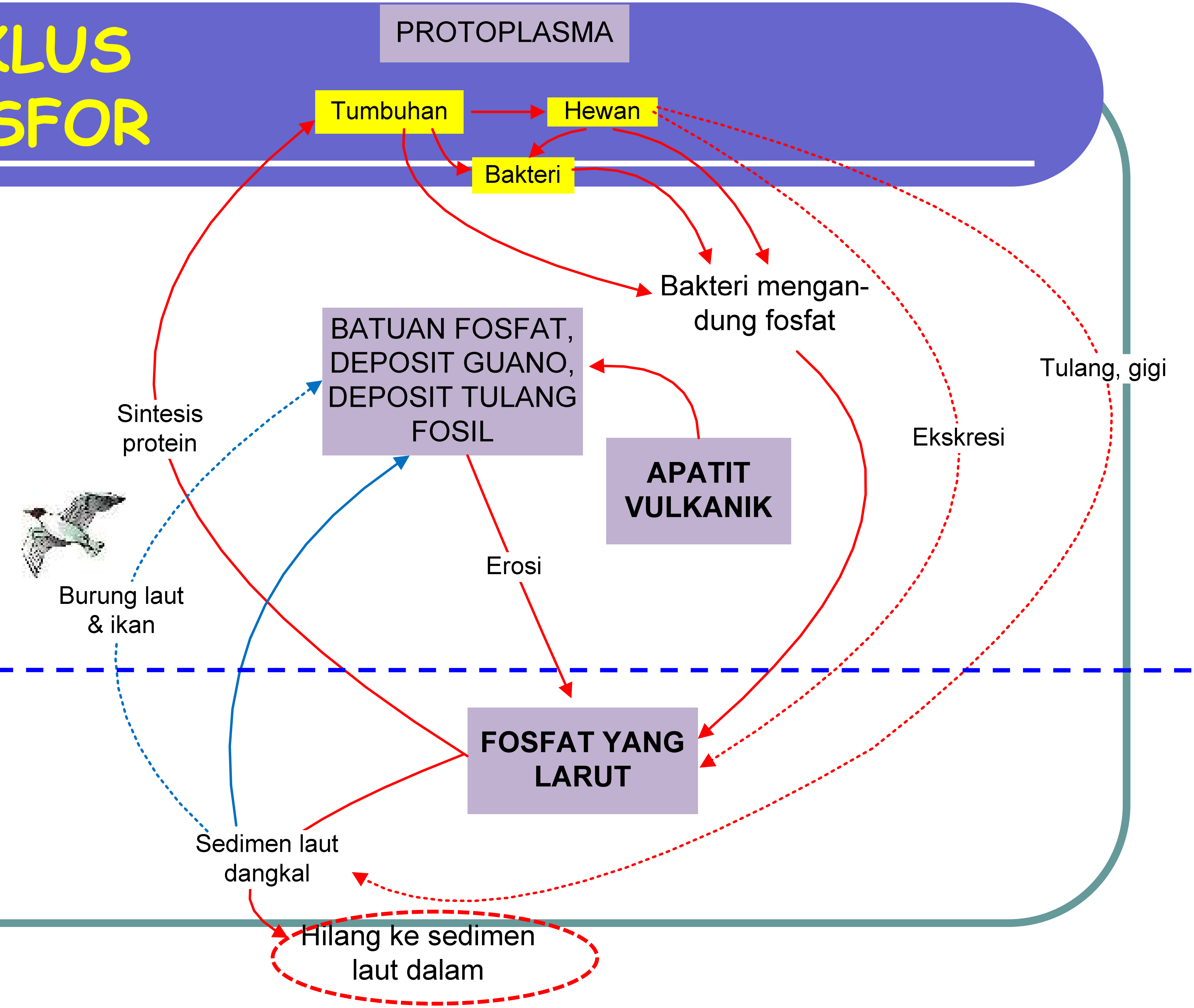
SIKLUS FOSFOR

- Siklus Fosfor lebih sederhana dari Siklus Nitrogen, terutama karena aksi bakteria untuk memecahkan ikatan organik fosfor lebih sederhana
- Laju dimana ikatan organik diubah jadi orthofosfat, yang merupakan ikatan fosfor yang digunakan tanaman, jauh lebih cepat dari nitrogen → karena pemecahan autolytic ikatan organik fosfor oleh enzym dan hanya diperlu-kan satu langkah oleh bakteri pemecah

SIKLUS FOSFOR

- Sumber fosfat yg terbesar adl BATUAN FOSFAT dan ENDAPAN GEOLOGIS yg terkikis/erosi, shg masuk ke ekosistem (daur fosfat)
- Peranan burung laut dan ikan sangat penting dalam mengangkat fosfat yg menuju laut/sedimen dalam (± 60.000 ton fosfor per tahun)
- Penambangan fosfat ± 1-2 juta ton per tahun dan kebanyakan tercuci dan hilang.
- Pengembalian fosfor ke daratan tidak dapat mengimbangi hilangnya fosfor ke laut dalam.

SIKLUS FOSFOR



Siklus Fosfor

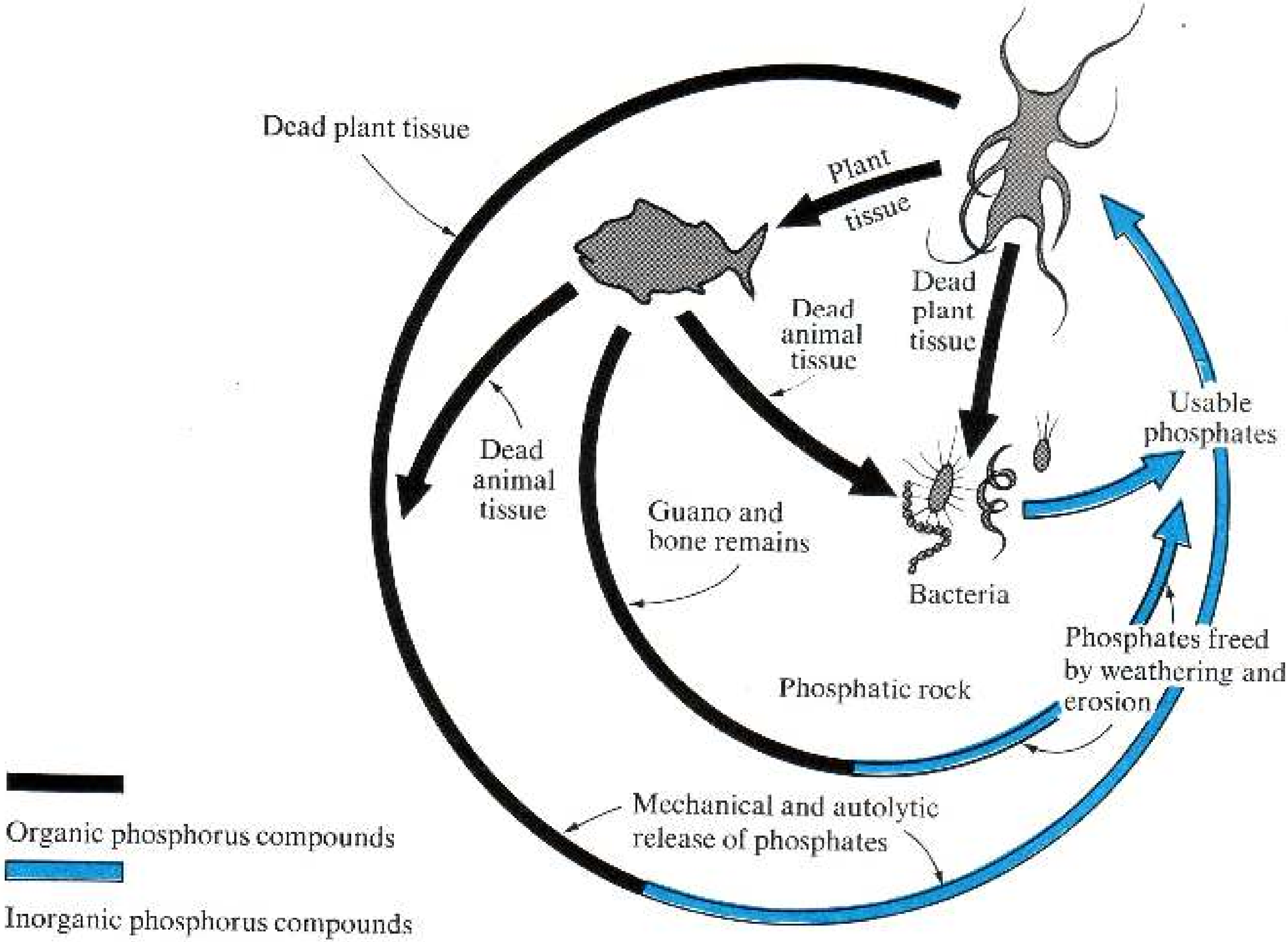


Figure 15–14 Phosphorus Cycle

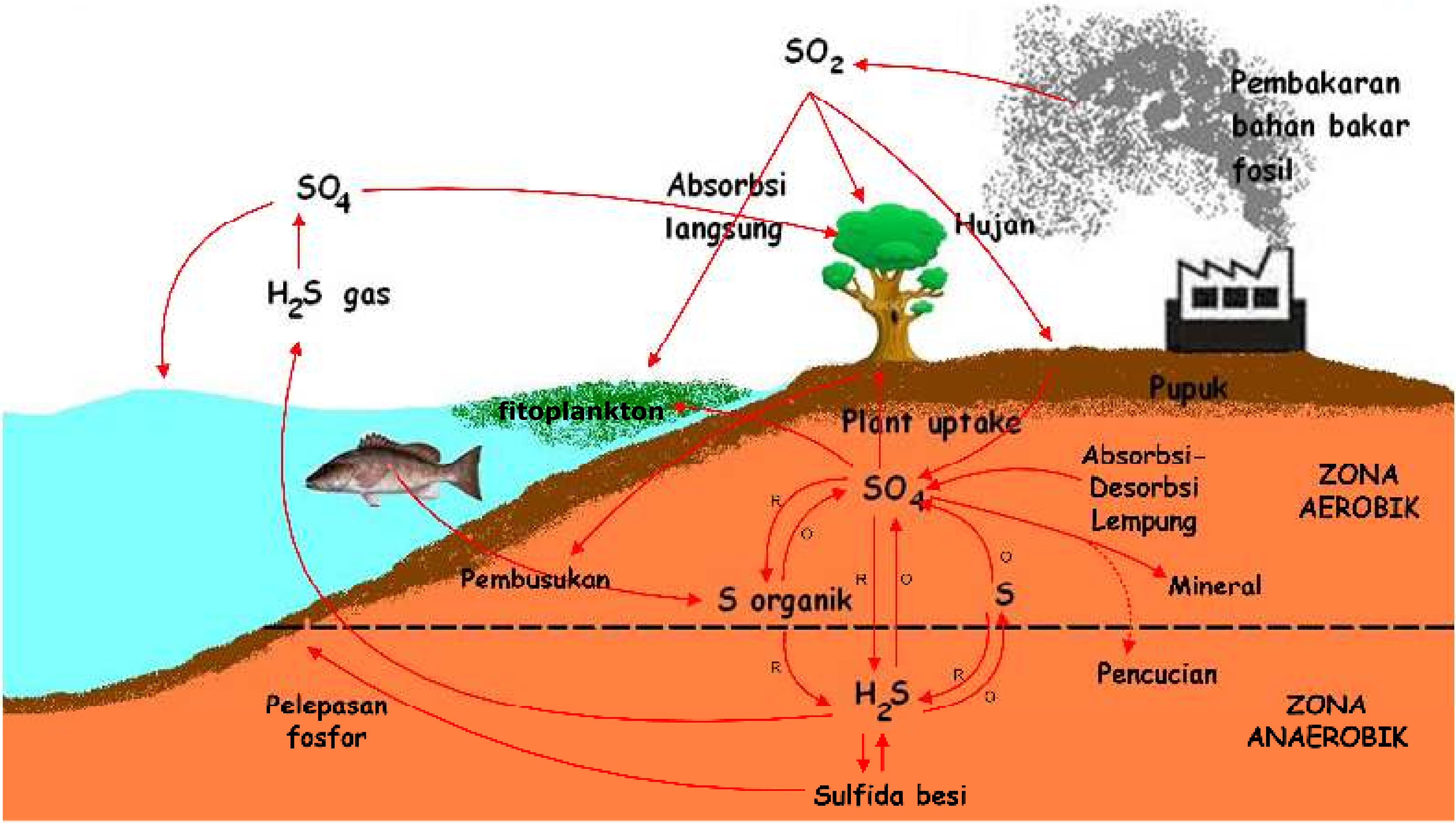
SIKLUS SULFUR

- Reservoir besar/utama sulfur terdapat pd atmosfer
- Daur sulfur menghubungkan UDARA, AIR, dan TANAH
- Oksida belerang (SO_2) dilepaskan ke udara pd pembakaran bahan bakar fosil, terutama batubara, merupakan komponen gangguan pencemaran udara dari industri

SIKLUS SULFUR

- Oksidasi-Reduksi merupakan kunci pertukaran antara kantong SO_4 dan sulfida besi
- Peranan kunci oleh mikroorganisme yg melakukan reaksi reduksi-oksidasi merupakan "penyembuhan/pemulihan" secara mikroba
- SO_2, NO, dan NO_2 merupakan komponen pencemar. SO_2 merusak proses fotosintesis, NO mengganggu respirasi

SIKLUS SULFUR



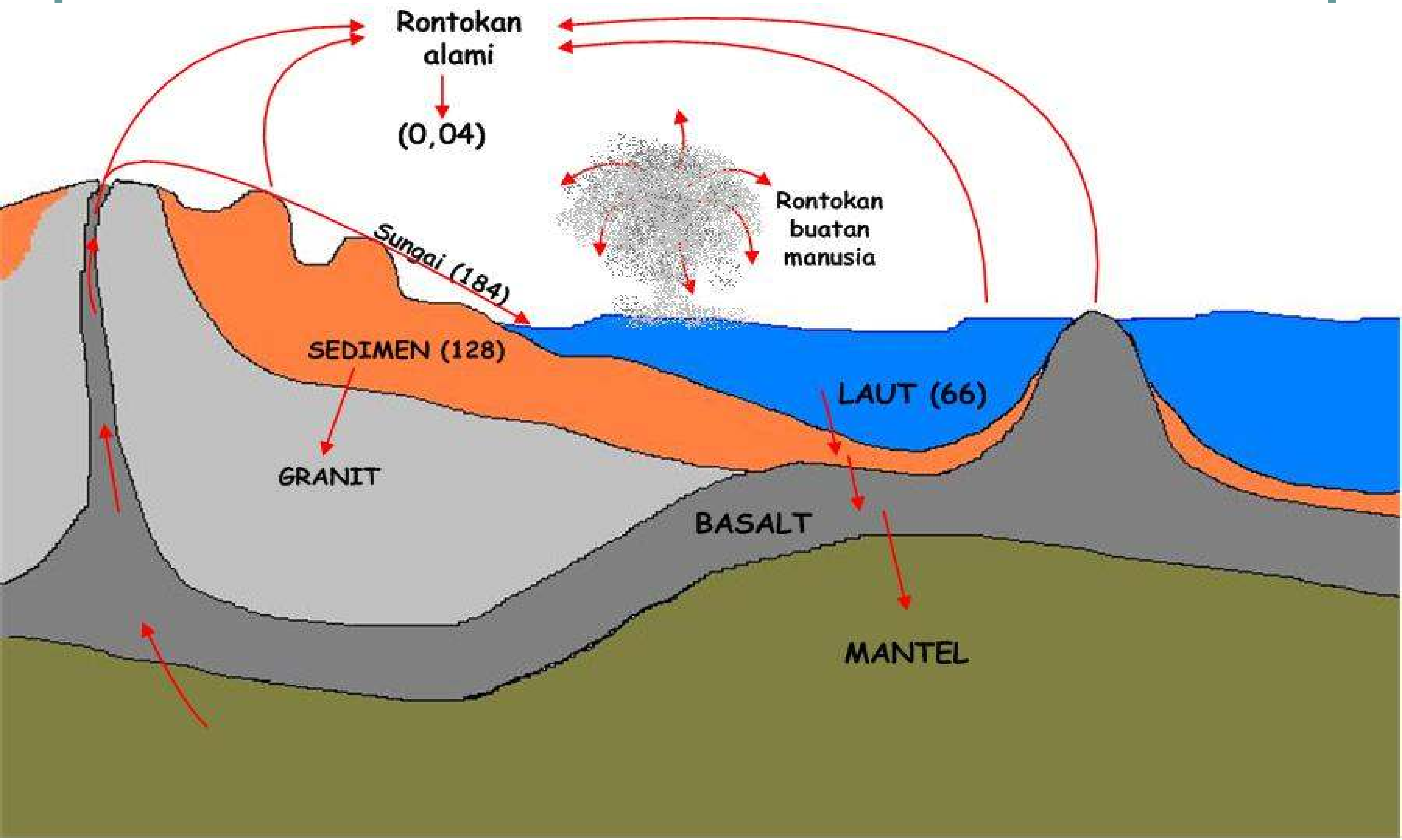
SIKLUS SULFUR

- Organisme yg berperan dlm daur sulfur:
  - $H_2S \rightarrow S \rightarrow SO_4$: bakteri sulfur tdk berwarna, hijau, dan ungu.
  - $SO_4 \rightarrow H_2S$: bakteri desulfovibrio
  - $H_2S \rightarrow SO_4$: bakteri thiobacilli
  - S organik $\rightarrow SO_4$ & H_2S : mikroorganisme aerob dan anaerob

DAUR SEDIMEN

- Kebanyakan unsur dan senyawa lebih terikat pada tanah daripada nitrogen, oksigen, CO_2 dan air → daurnya mengikuti pola daur sedimen dasar.
- Erosi, sedimentasi, pembentukan gunung, dan kegiatan vulkanis, serta transport secara biologi merupakan perantara utama yg mempengaruhi peredarannya.

DAUR SEDIMEN



DAUR SEDIMEN

- Benua Asia (benua dgn peradaban tertua & paling intensif tekanan manusianya) kehilangan paling banyak tanah.

Tabel arus sedimen dari benua ke lautan per tahun

No.	BENUA	DAERAH DRAINASE (10^6 mil^2)	PELEPASAN (ton/mil^2)	SEDIMEN TOTAL (10^9 ton)
1	Amerika Utara	8,0	245	1,96
2	Amerikan Selatan	7,5	160	1,20
3	Afrika	7,7	70	0,54
4	Australia	2,0	115	0,23
5	Eropa	3,6	90	0,32
6	Asia	10,4	1.530	15,91

Daur Unsur-Unsur non Esensial

- Pola daur unsur non esensial sama dgn pola daur unsur esensial; sebagian besar terlinat pada unsur sedimen
- Banyak dari elemen non esensial terkonsentrasi dalam jaringan organisme krn kesamaannya scr kimiawi dgn elemen tertentu, spt Hg dan Pb.

Daur Unsur-Unsur non Esensial

- Unsur-unsur non esensial dpt menimbulkan masalah ekologi, spt:
  - Bahan-bahan radioaktif
  - Limbah industri berupa logam berat
- Contoh:
  - Stronsium (Sr) merupakan unsur radioaktif yg sangat berbahaya bagi manusia dan vertebrata lainnya. Sr bersifat spt kalsium → dpt berhubungan erat dgn jaringan pembentuk darah yg sangat peka thd kerusakan akibat radioaktif (dapat menimbulkan kanker)

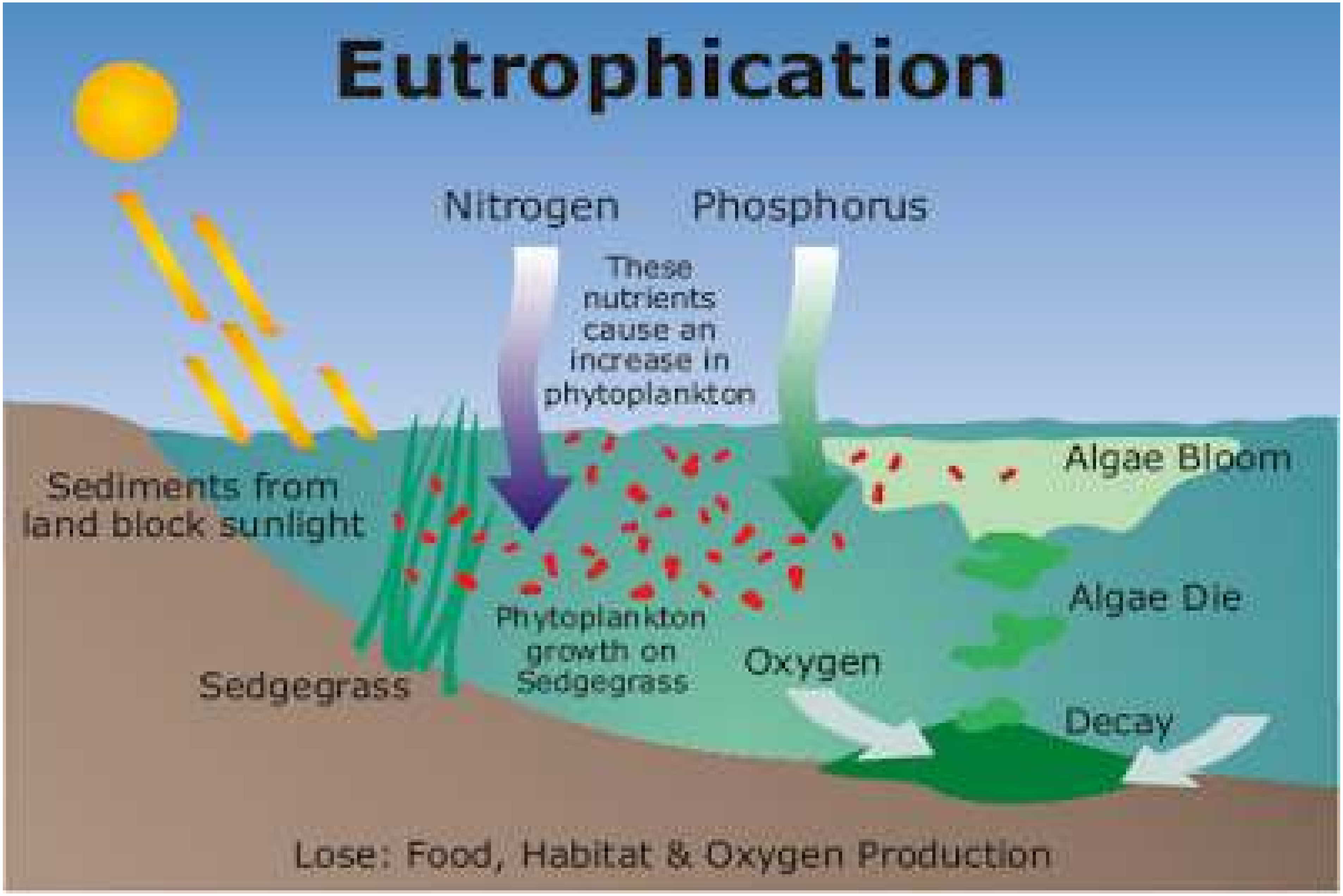
Daur Hara Organik

- Organisme heterotrof & beberapa autotrof (algae) memerlukan beberapa macam vitamin dan nutrien lain dari lingkungannya.
- Sebagian besar nutrien organik berasal dari organisme (biotik)
- Konsentrasi nutrien organik di alam sangat sedikit (nutrien mikro) → Faktor Pembatas. Contoh: B_{12} (di laut)
- Cara mengukur kadar mikronutrien dengan metode <u>bioassay</u>

Eutrofikasi

- **Eutrophication** refers to an excessive amount of nutrients in a body of water, usually caused by runoff of nutrients (mainly phosphorous in freshwater and nitrogen in saltwater) from the land, which causes a dense growth of plant life, leading to a decrease in oxygen supply, which causes the death of animals.

Eutrofikasi krn alam



Eutrofikasi krn antropogenik

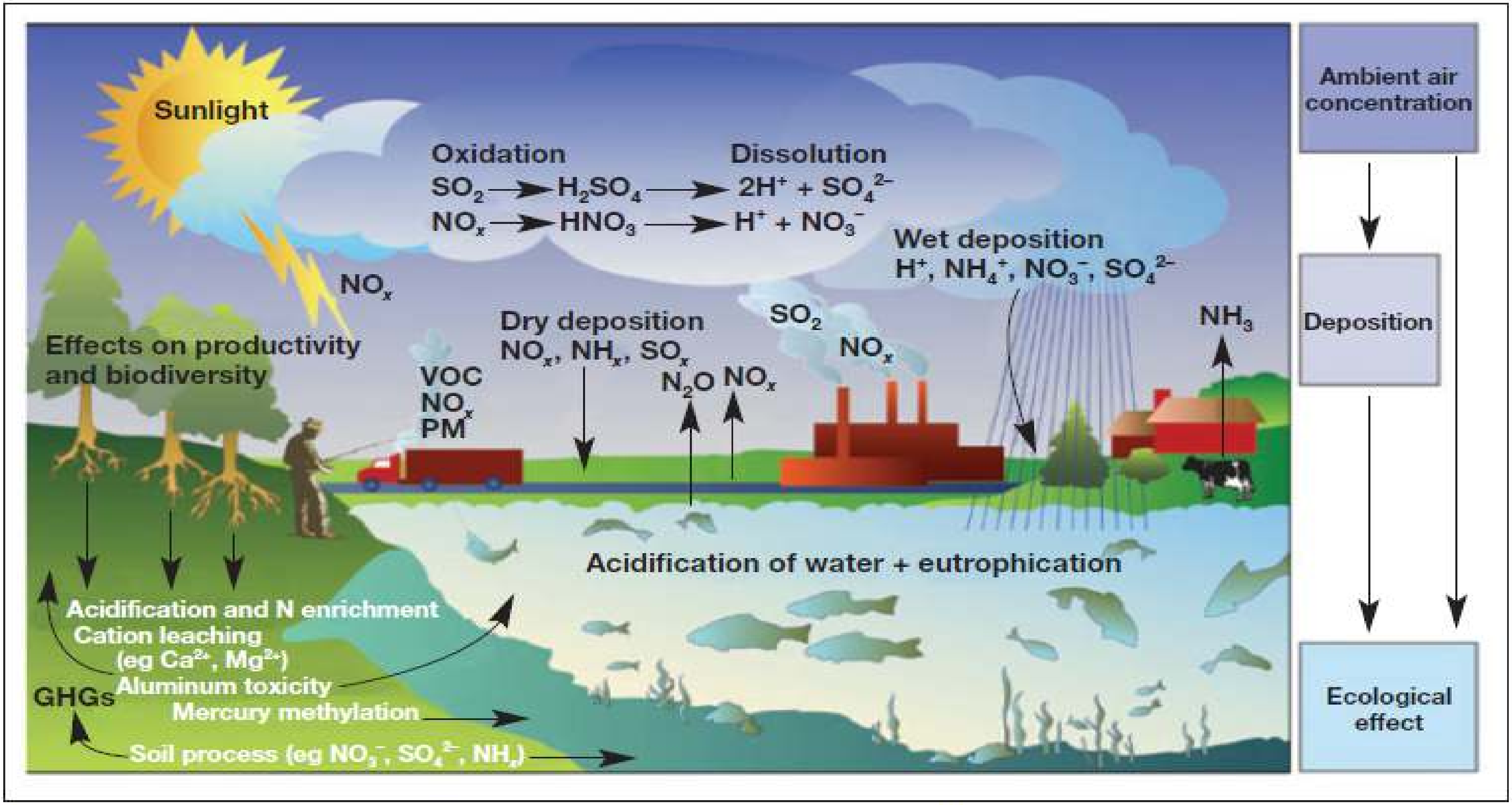
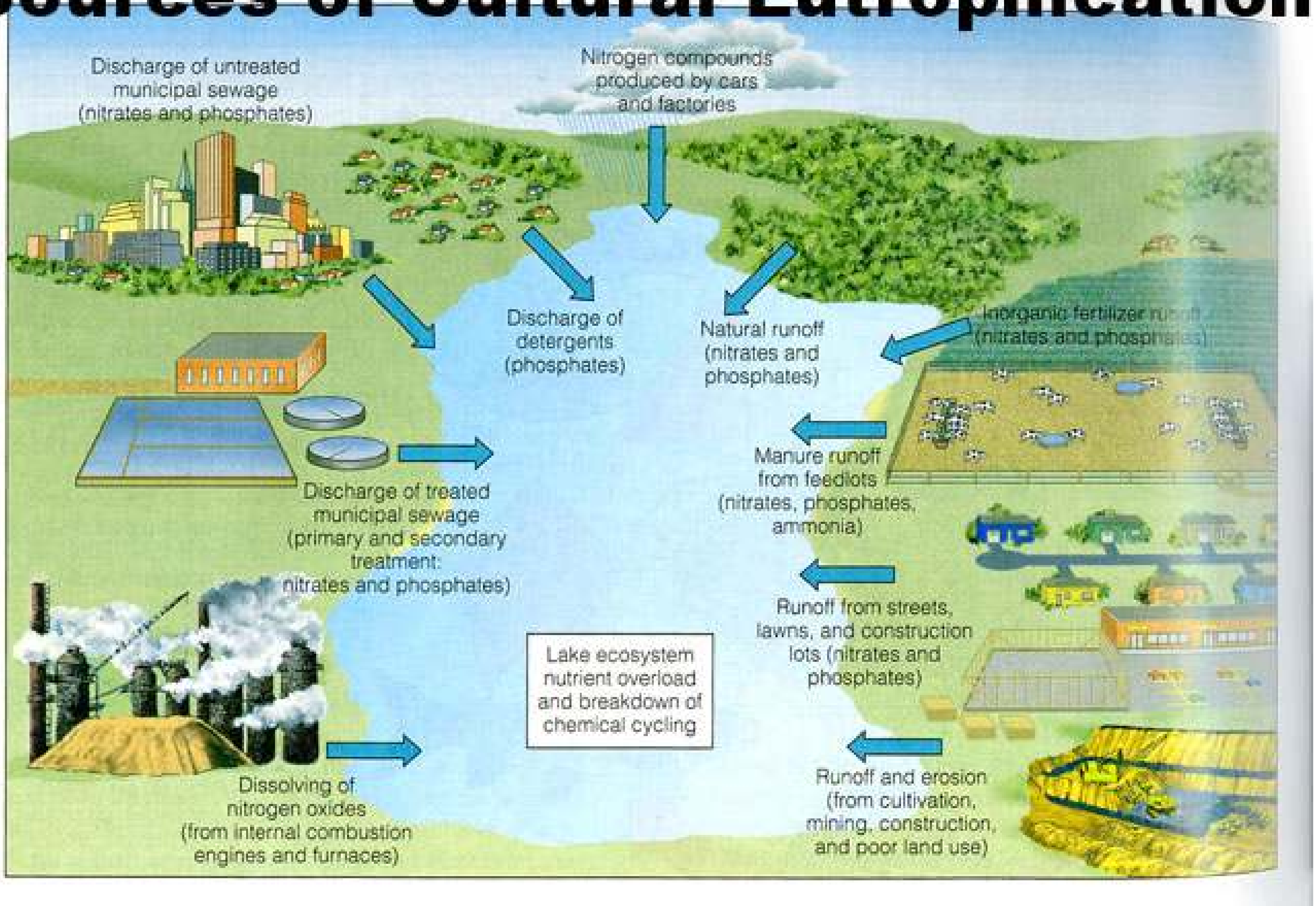


Figure 1. *Simplified diagram of the ecological effects caused by nitrogen and sulfur air pollution. VOC = volatile organic compound; PM = particulate matter; GHGs = greenhouse gases.*

Sources of Cultural Eutrophication



Red Tides

- Red tide is a common name for a phenomenon known as an algal bloom (large concentrations of aquatic microorganisms) when it is caused by a few species of dinoflagellates and the bloom takes on a red or brown color.
- *Red tide* is a colloquial term used to refer to one of a variety of natural phenomena known as *harmful algal blooms* or *HABs*. The term *red tide* specifically refers to blooms of a species of dinoflagellate
- Red tides are events in which estuarine, marine, or fresh water algae accumulate rapidly in the water column, resulting in coloration of the surface water. It is usually found in coastal areas.
- Certain species of phytoplankton, dinoflagellates, contain photosynthetic pigments that vary in color from green to brown to red.

Red tides


WARNING . . .
TOXIC SHELLFISH
SHELLFISH FROM THIS AREA ARE UNSAFE TO EAT DUE TO PARALYTIC SHELLFISH TOXIN
DO NOT EAT CLAMS, OYSTERS, MUSSELS OR SCALLOPS.


NEWS TV
RED TIDE
BENTAHAN NG SHELLFISH, APEKTADO DAHIL SA RED TIDE SA BATAAN AT PANGASINAN
SA BUROL NG KANYANG BAYAW NA SI REP. IGGY ARROYO, INAANTABA

Logam Berat

- Air sering tercemar oleh komponen anorganik, a.l. logam berat
- Logam berat yang mencemari antara lain merkuri (Hg) , timbal (Pb) , arsenik (As), cadmium (Cd), cromium (Cr) dan nikel (Ni)
- Logam berat jika terakumulasi lama dalam tubuh menyebabkan keracunan pada mahluk hidup → kematian

Contoh: tragedi Minamata (Jepang 1953)

1953 Minamata, Japan

A chemical factory was dumping mercury into a nearby bay, which led into the sea and contaminated the fish with mercury. Many people died because of the poisoning. Birth defects were common.

Mercury Cycle

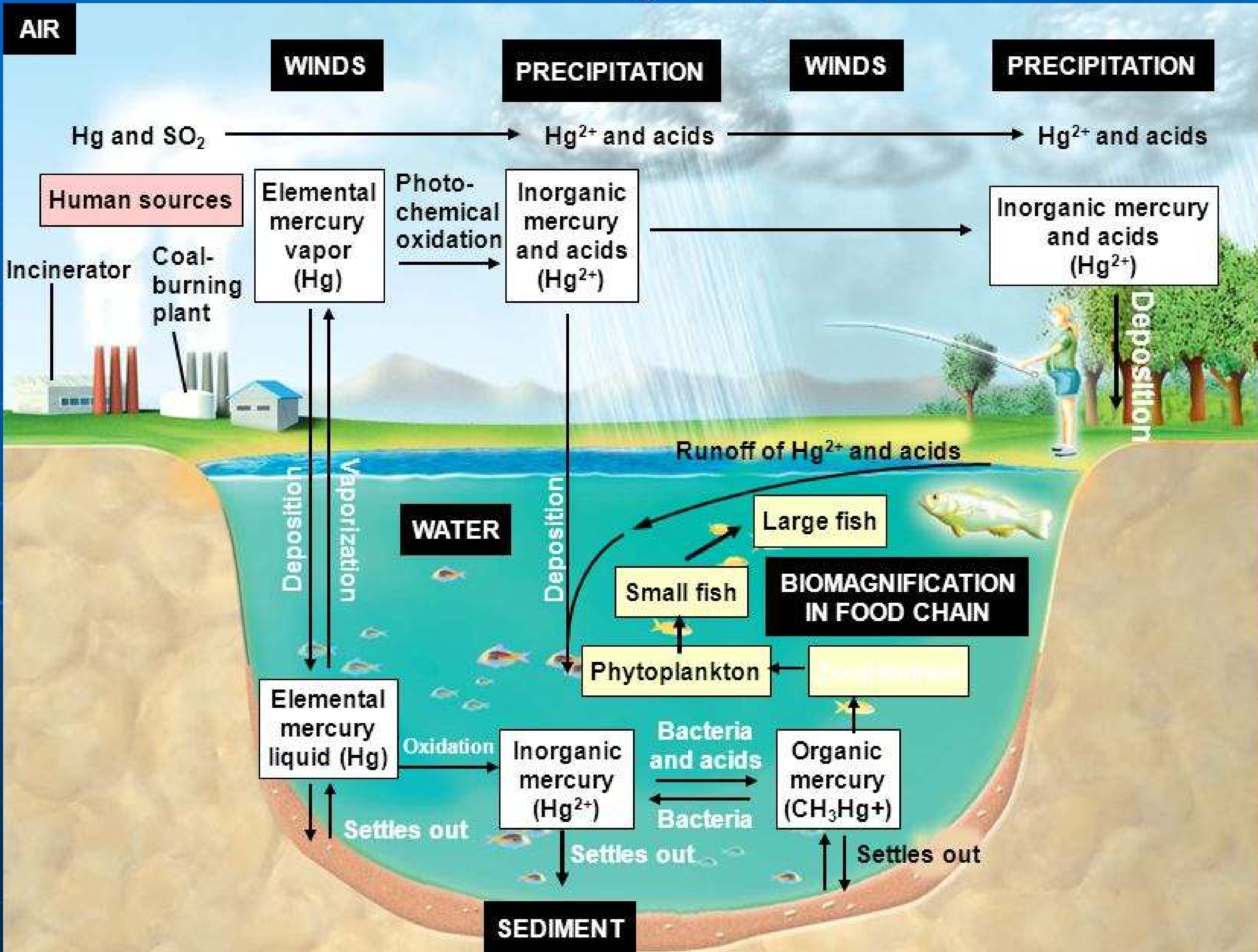
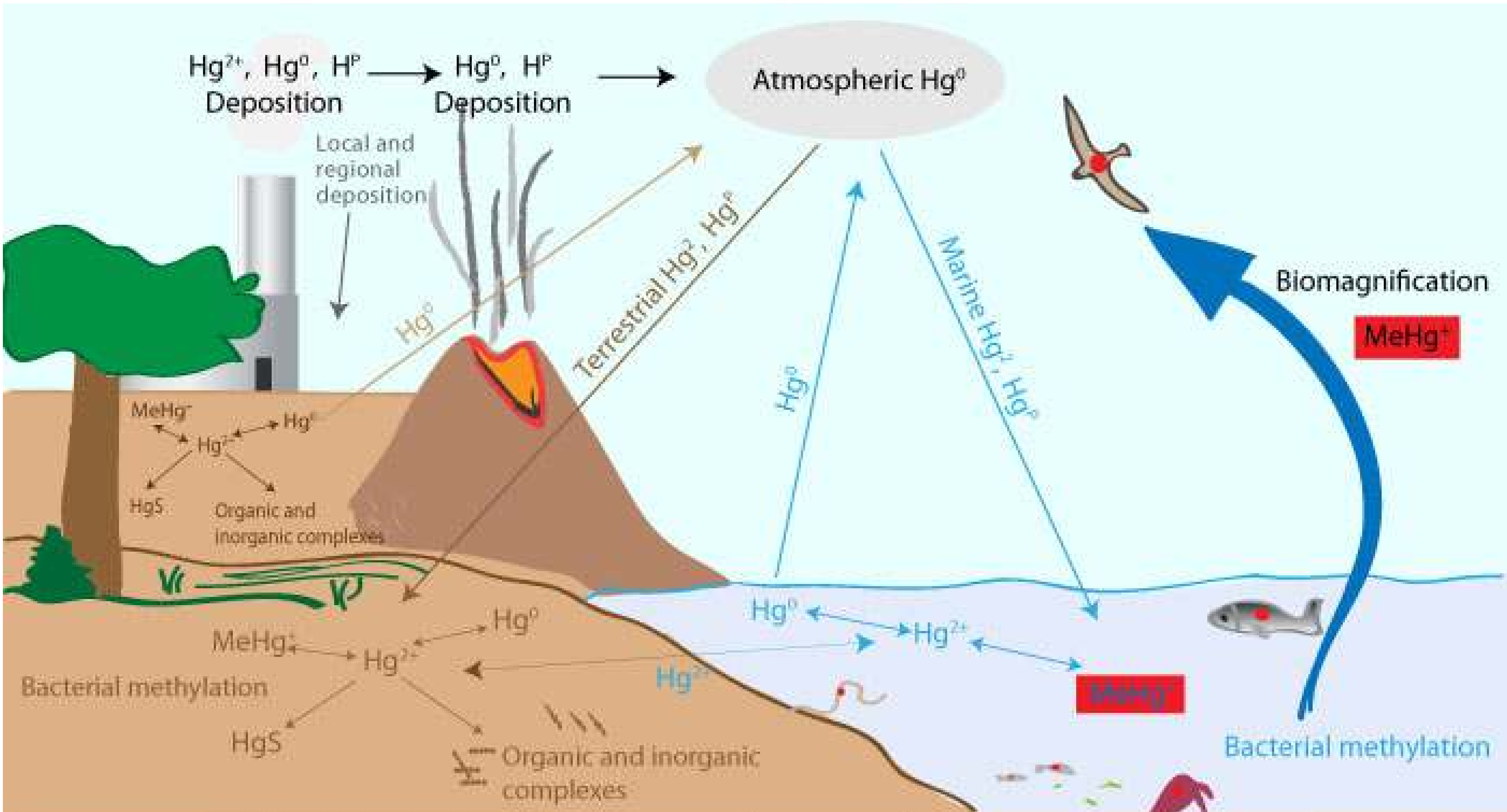


Fig. 17-22, p. 408

Metil merkuri



Elemental Mercury - Hg^0 | Reactive Mercury - Hg^{2+} | Particulate Mercury - Hg^P | Cinnabar - HgS | Methylmercury - MeHg | Methylmercury Accumulation -

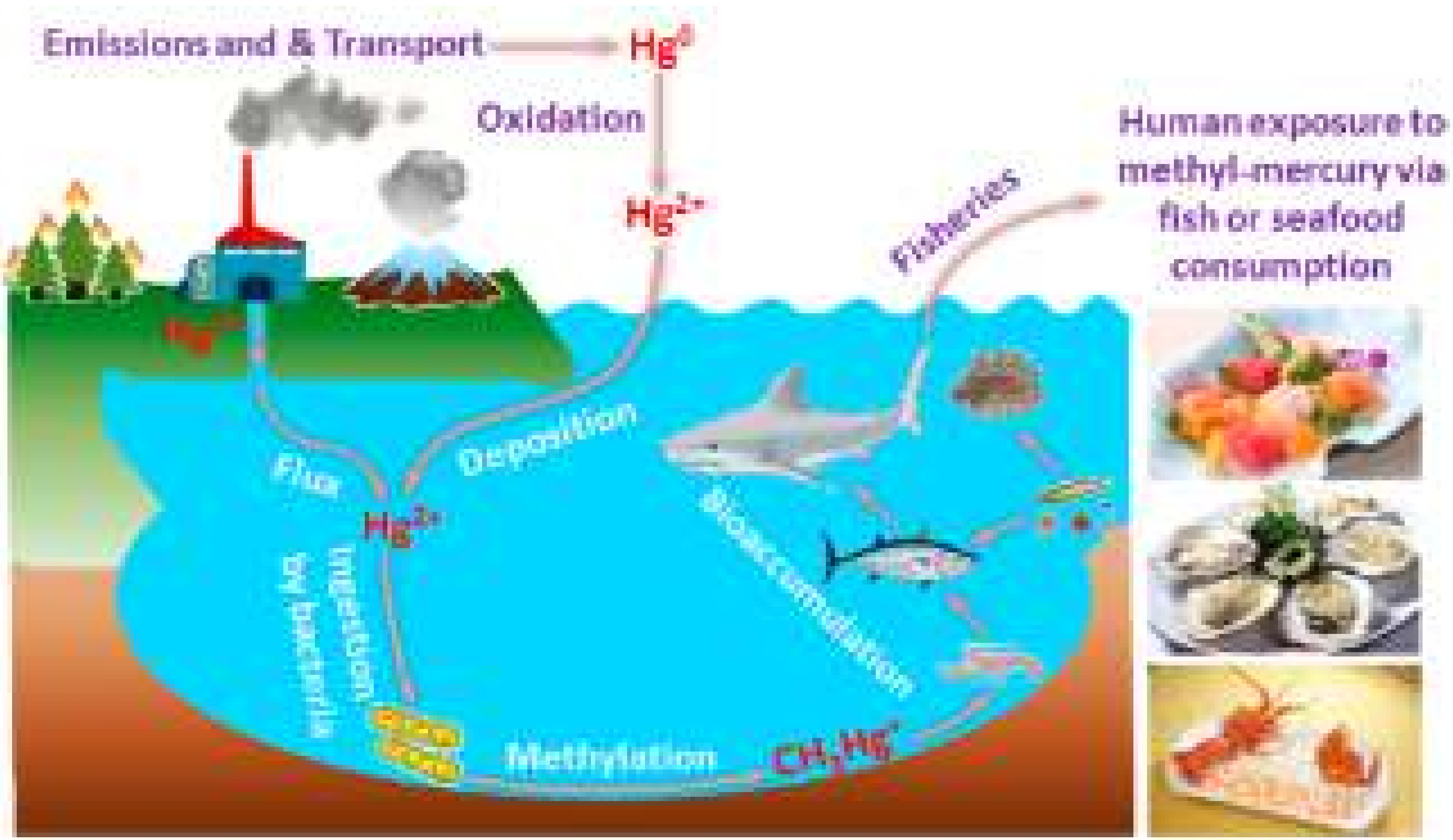
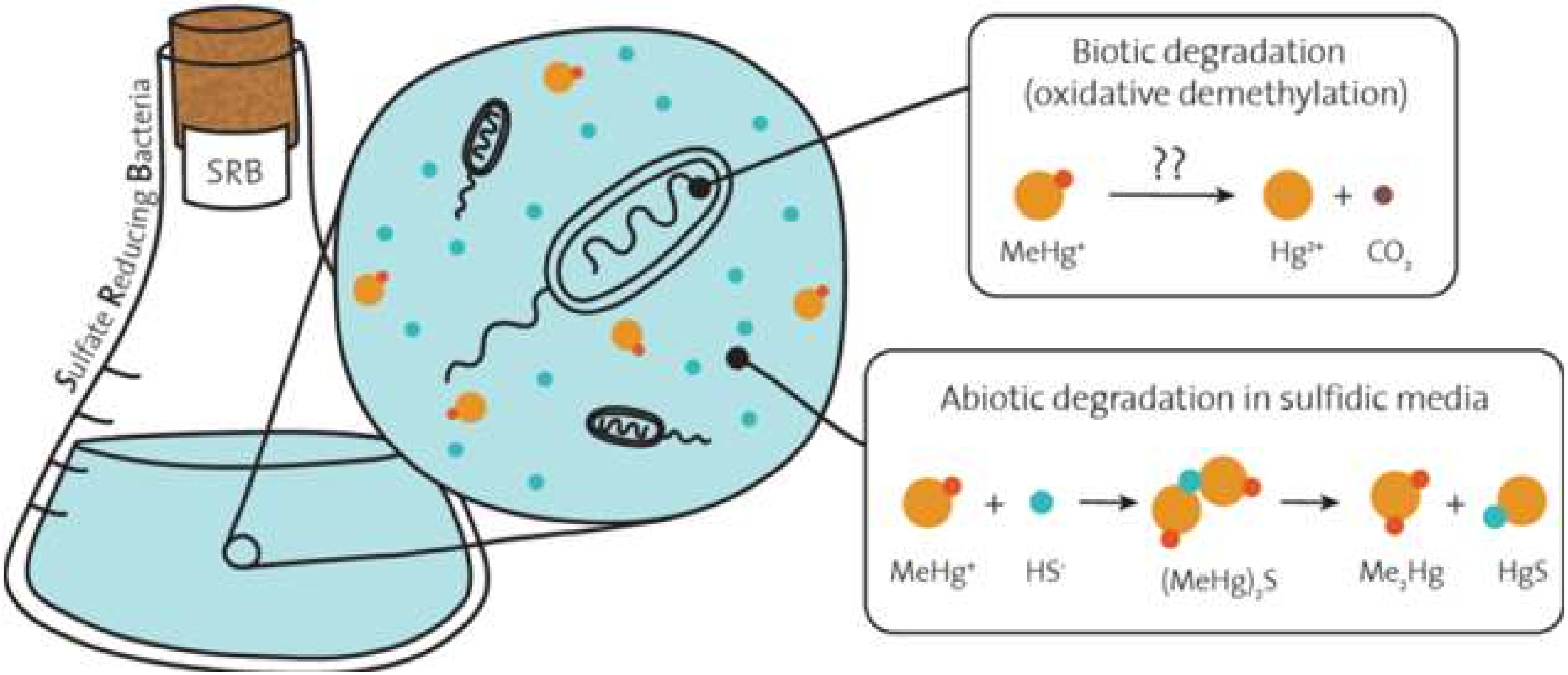


Figure 1. Schematic illustration of CH_3Hg^+ generating and entering human diet via the food chain. (Deng *et a*l., 2015)



Heavy metals are toxic, but sometimes their organometallic compounds are worse. In this respect, methylmercury ($MeHg^{+}$) represents an excellent example: the detrimental health and environmental effects associated with mercury (Hg) pollution are in fact caused by $MeHg^{+}$, and not by the metal itself.
Methylmercury is produced in the aquatic environment by archea and anoxic bacteria, which use inorganic mercury as a starting substrate. Once produced, $MeHg^{+}$ enters the food-web and accumulates in organisms such as fish and seafood, which represents the main methylmercury exposure pathway for the human beings.
Due to its high neurotoxicity, many efforts have been devoted to improve our knowledge on the environmental fate of methylmercury. In this context, identify and characterize $MeHg^{+}$ degradation mechanisms represent an important step, as the degradation processes will directly affect methylmercury concentrations in the environment, thus the dose at which we are exposed.

So far, four different $MeHg^+$ degradation pathways have been identified. The so-called oxidative demethylation involves the degradation of $MeHg^+$ to inorganic mercury and carbon dioxide by anaerobic bacteria. Differently from the other three processes, which are relatively well understood, many doubts still remain on the details of this pathway despite almost 30 years of scientific investigations. So many, in fact, to bring some researchers back to the literature with a big question to be answered: is oxidative demethylation a real process, or it is just an experimental artifact?

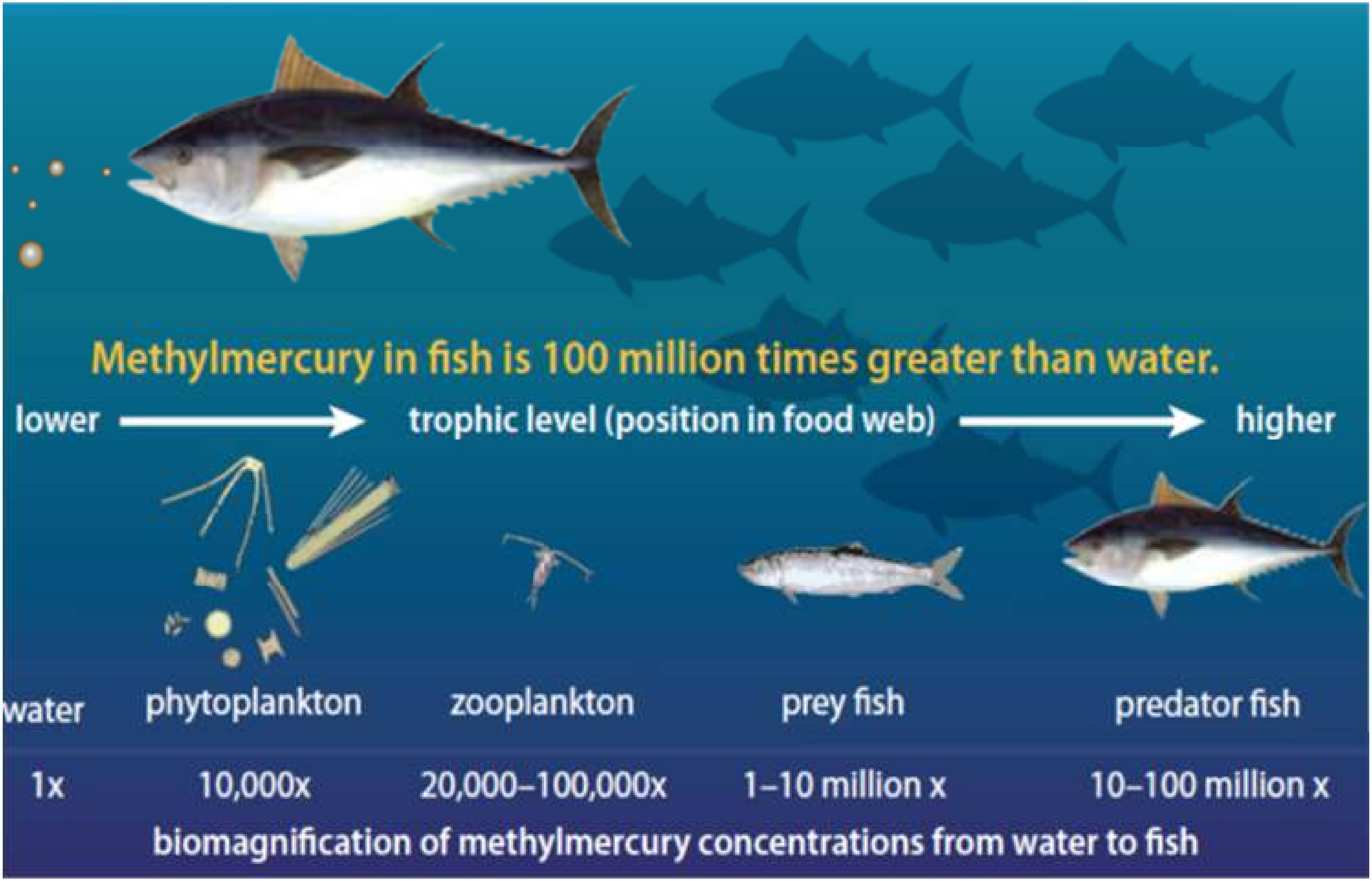
Based on the available literature on methylmercury chemistry and biogeochemistry, Kanzler *et al.* hypothesized that a simple abiotic process could be responsible for the $MeHg^+$ degradation that have been observed in the presence of sulfate-reducing bacteria, the microorganisms that are believed to perform oxidative demethylation. The proposed reaction involves the formation of a binuclear complex, bis(methylmercury) sulphide ($(MeHg)_2S$), which can degrade to insoluble cinnabar (HgS) and dimethylmercury (Me_2Hg), a volatile compound.

$$2MeHg^+ + HS^- \rightleftharpoons (MeHg)_2\,S + H^+ \rightarrow Me_2Hg + HgS$$

Several factors influence the thermodynamics and the kinetics of this reaction, including the solution pH and the concentrations of the two precursors, methylmercury and hydrogen sulfide. Using a combination of experimental and computational approaches, Kanzler *et al.* developed a model that allows the prediction of both $MeHg^+$ speciation (*i.e.*, the position of the first equilibrium) and dimethylmercury formation rates as a function of the chemical composition of the medium.

(Rilley, 2018) https://blogs.rsc.org/em/2018/07/24/oxidative-demethylation-biotic-or-abiotic-methylmercury-degradation/?doing_wp_cron=1655809522.4264400005340576171875

Biomagnifikasi metil mercuri



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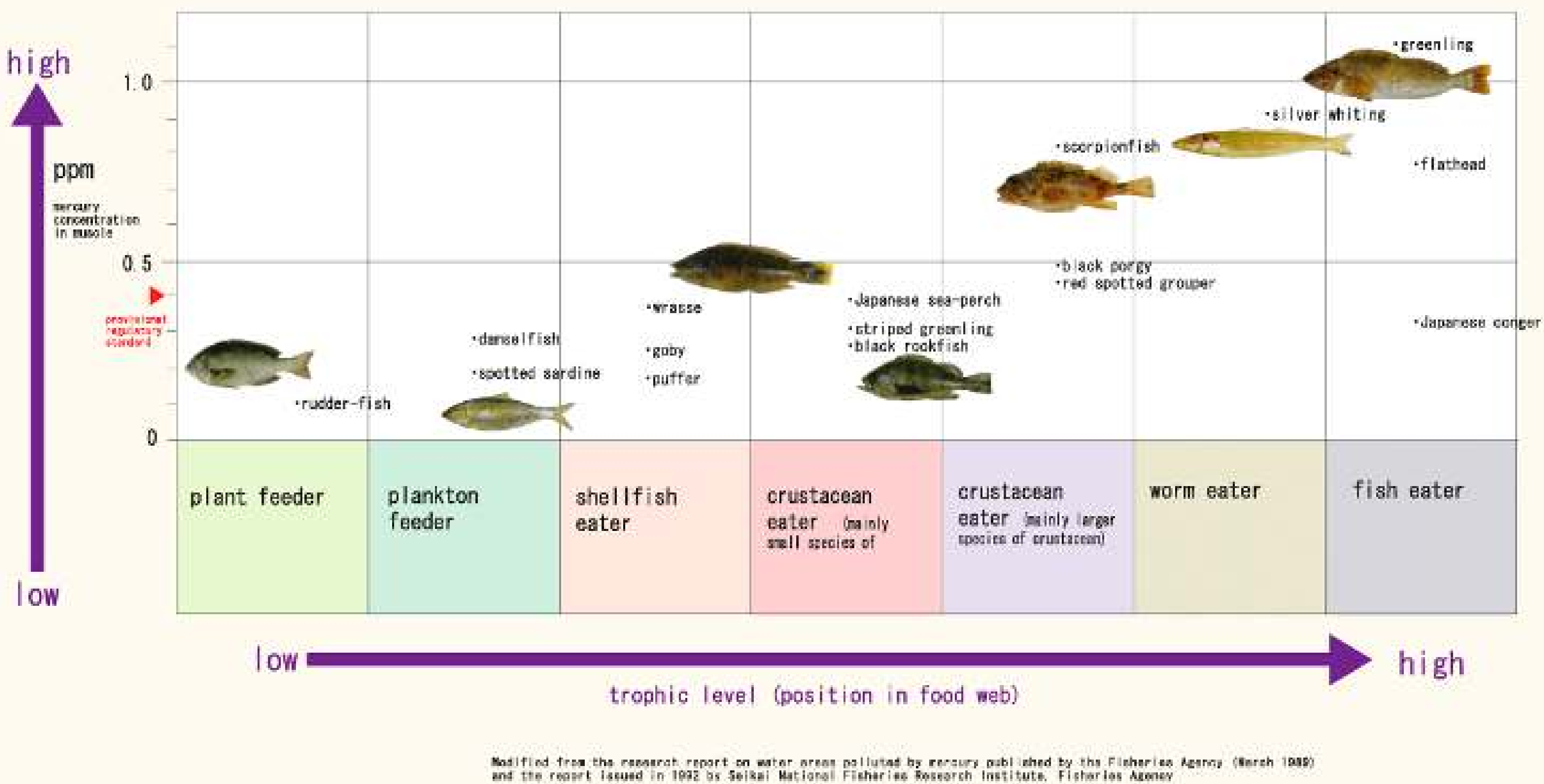


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