



NPTEL ONLINE CERTIFICATION COURSES

Introduction to Environmental Engineering and Science – Fundamentals and Sustainability Concepts

Dr. Brajesh Kumar Dubey
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IIT Kharagpur

Week-3 Topics

Ecology, Population & Environmental Chemistry

Lecture 11 : Ecology

CONCEPTS COVERED

Topics to be covered this week

- Ecology,
- Population
- Environmental Chemistry

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What is Ecology?

The scientific study of interactions between different organisms and between organisms and their environment or surroundings



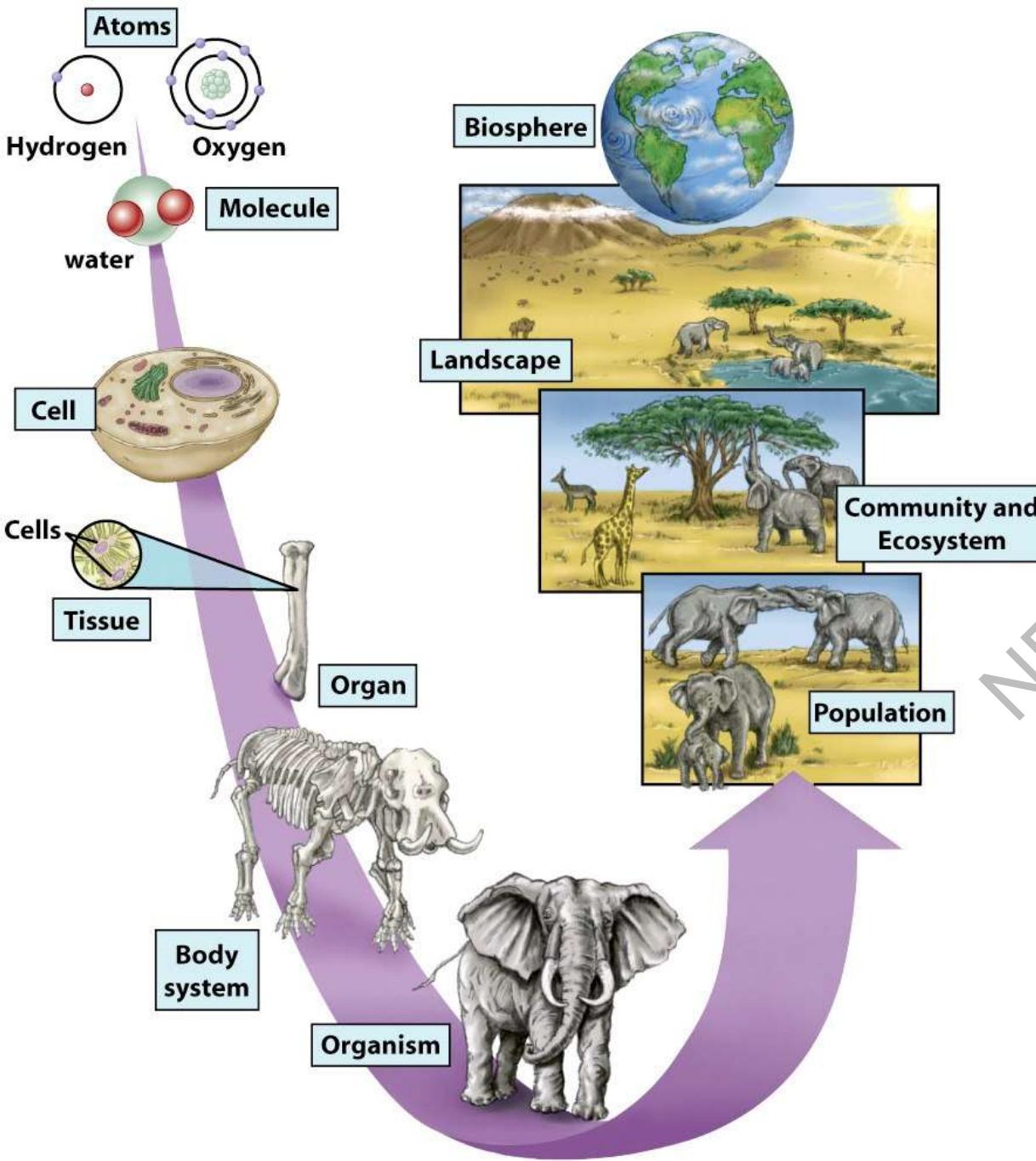
•**Biotic**

- Living component of the environment
- Ex: birds, insects

•**Abiotic**

- Nonliving or physical components of the environment Ex: light, oxygen

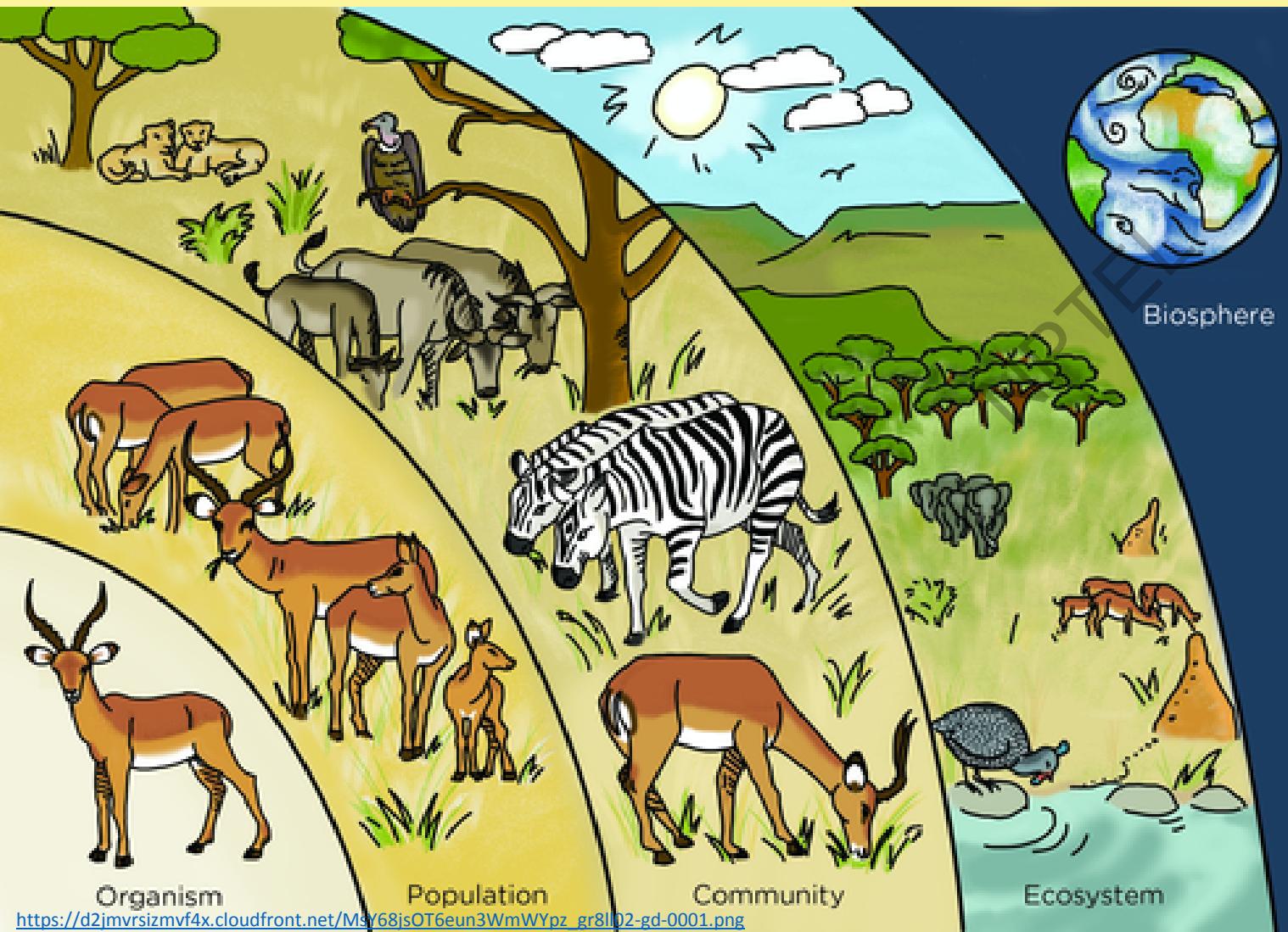




Levels

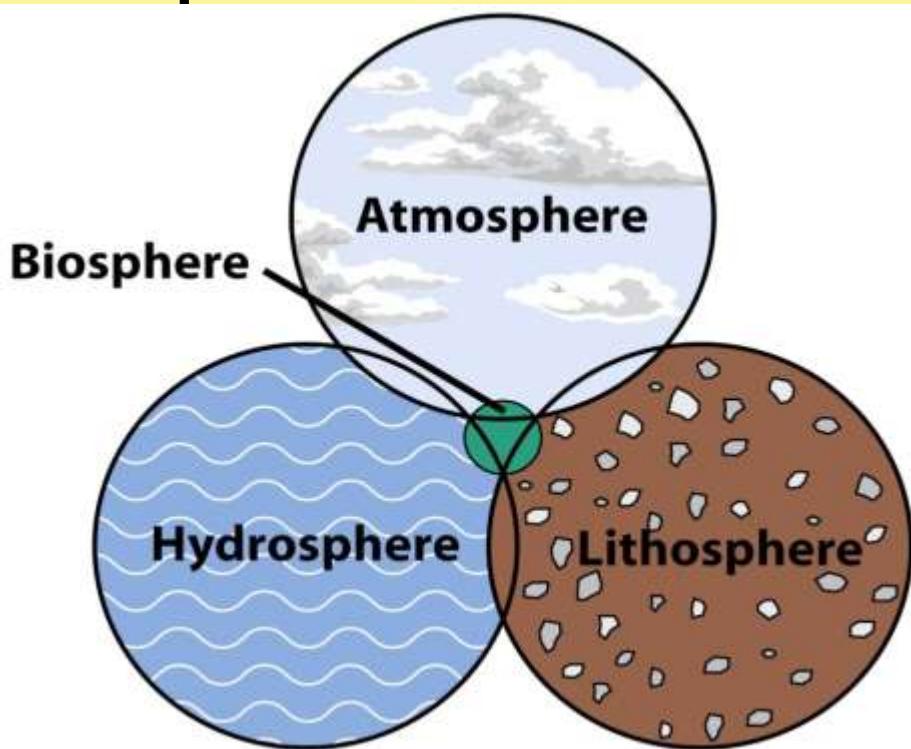
Starts with the atom, which combines to form a molecule -> cells -> tissues -> organs etc.

What is the difference between Ecosystem, Community and Population?



Landscape Ecology

- Landscape ecology is the study of the interactions between the temporal and spatial aspects of a landscape and the organisms within it.
- A sub discipline that studies ecological processes that operate over large areas
- Landscape –encompasses larger area and several ecosystems
- Biosphere –the whole earth



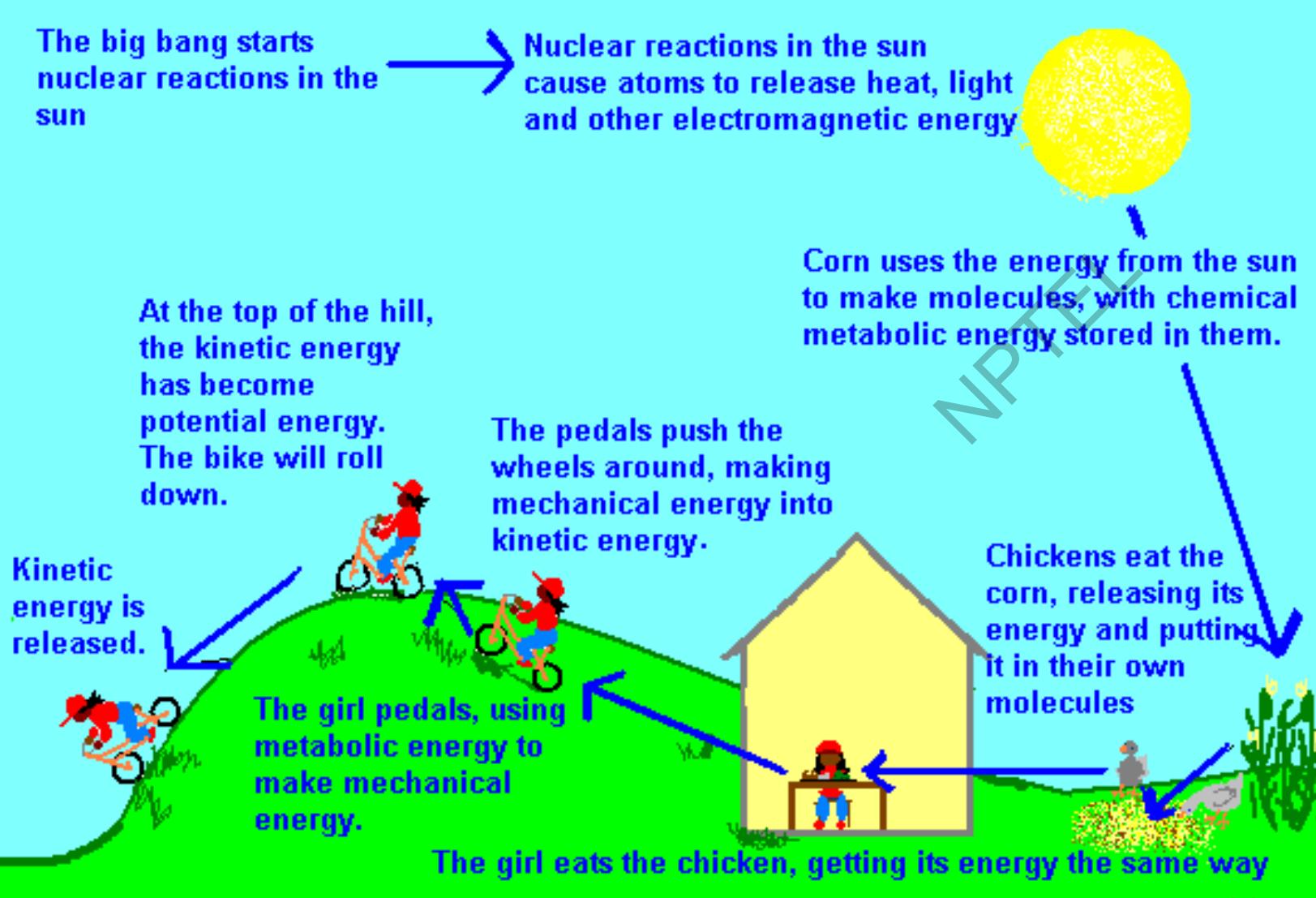
What is energy?

- The capacity or ability to do work
- **Energy exist in different forms**
 - Chemical, radiant (light), thermal (heat), mechanical, nuclear, electrical
- **Units**
 - Kilojoules (kJ)
 - Kilocalories (kcal)
 - $1 \text{ kcal} = 4.184 \text{ kJ}$

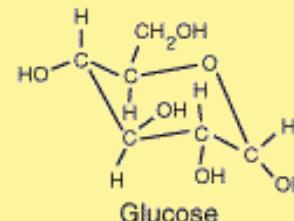
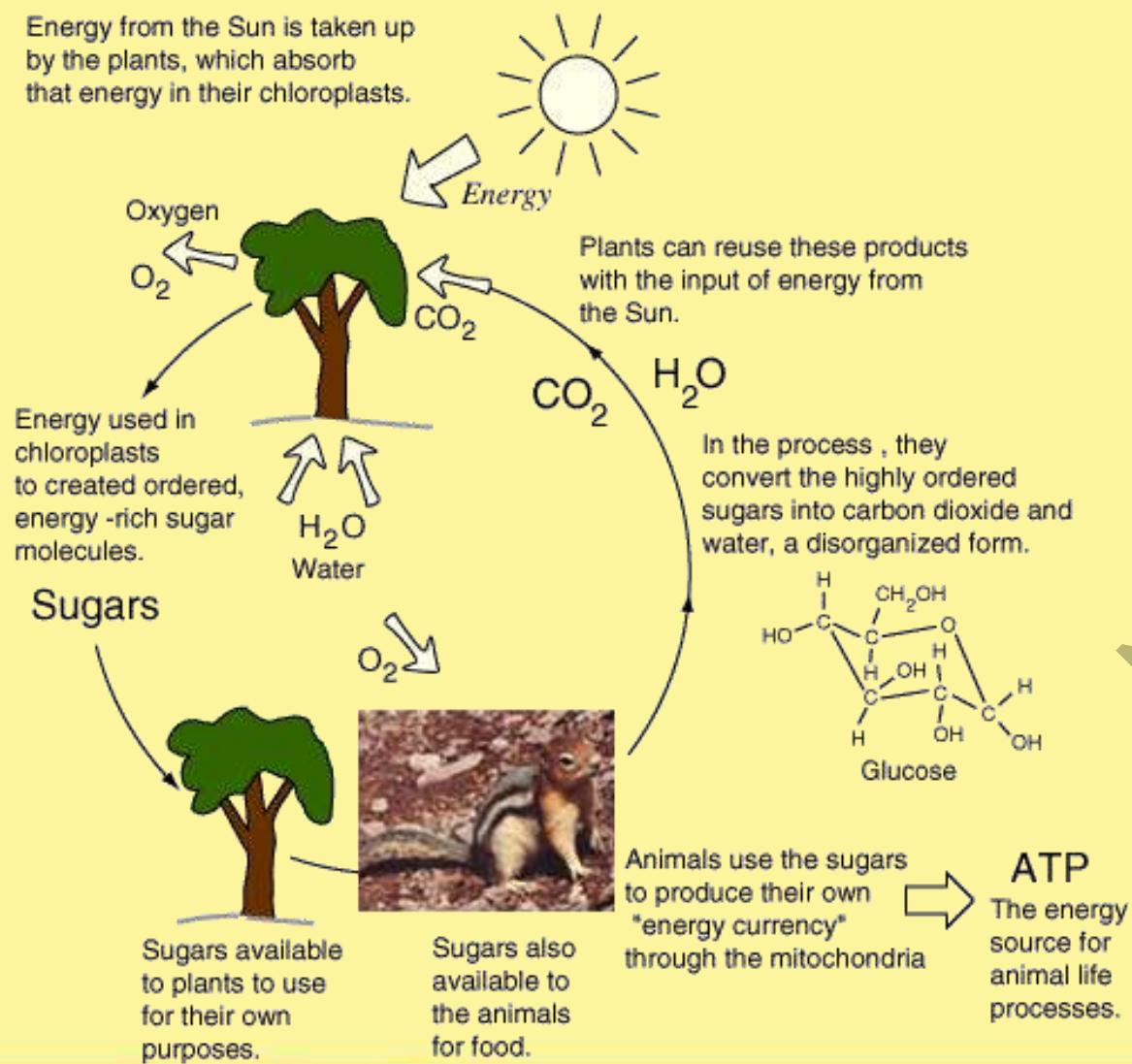
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Where does energy come from? Where does energy go?



Energy from the Sun is taken up by the plants, which absorb that energy in their chloroplasts.



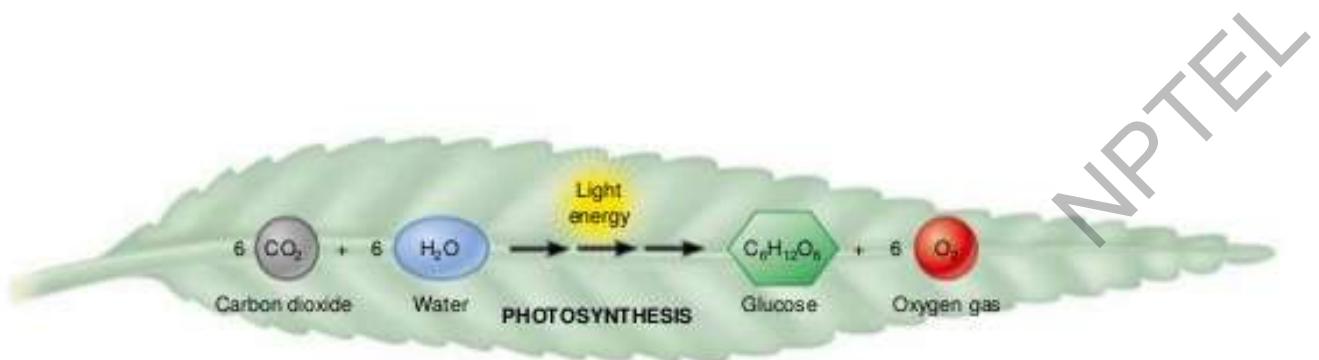
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Sugars available to plants to use for their own purposes.

Sugars also available to the animals for food.

ATP

- Photosynthesis is the process by which certain organisms use light energy to make sugar and oxygen gas from carbon dioxide and water
- The net equation is cellular respiration run *backwards*



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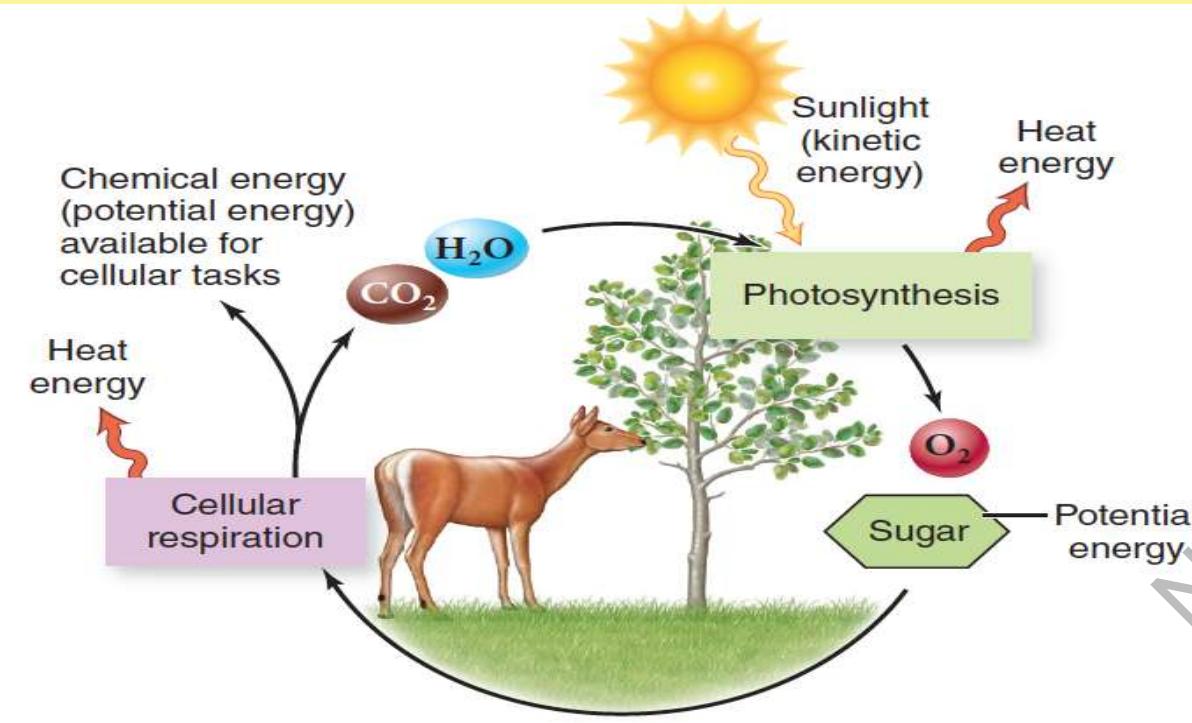


- **1st Law of Thermodynamics –**
energy can change forms, but is not created or destroyed
- **2nd Law of Thermodynamics –**
- **“Entropy Rules!”**
amount of usable energy decreases as energy changes forms
- **1st Law deals with quantity of energy,**
- **2nd Law with quality of energy.**

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Energy Is Converted from One Form to Another

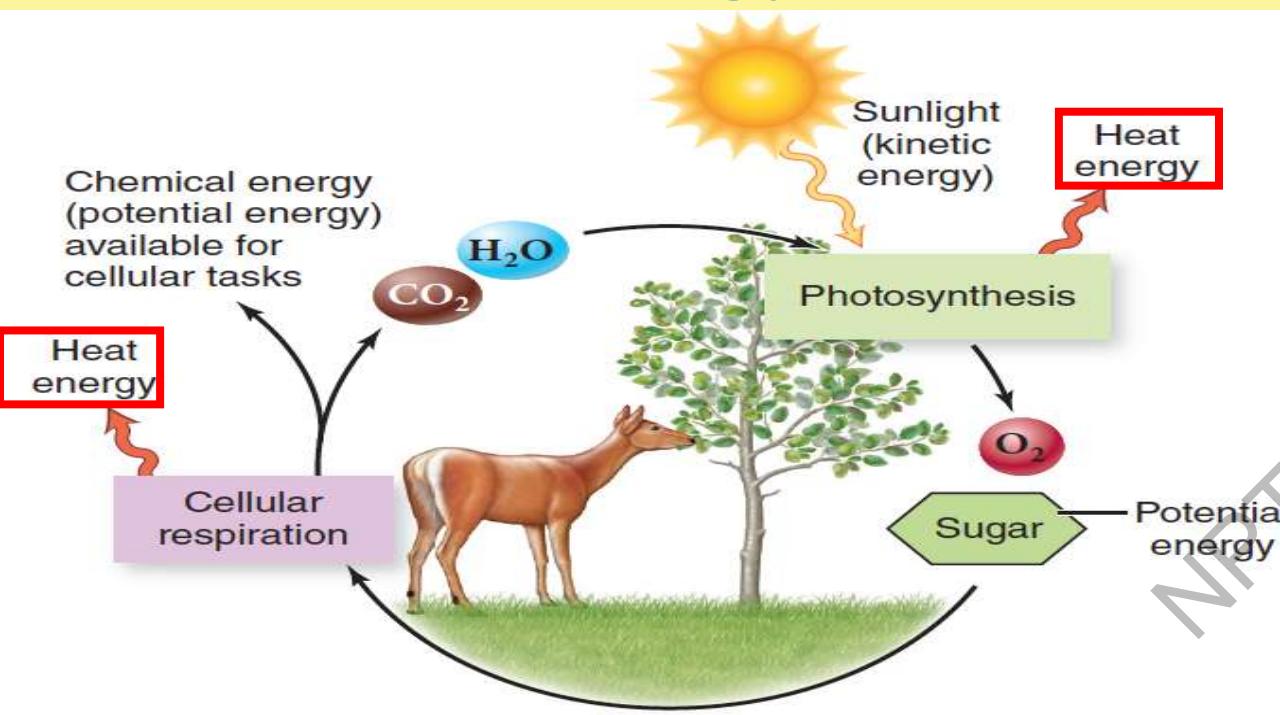


First law of thermodynamics: energy is never created nor destroyed.

Total amount of energy in the universe is constant.



Energy Transformations Are Inefficient



- Notice that heat energy is lost at each step. Heat energy is disordered and cannot be converted back to a useful form of energy.
- Since heat energy is constantly being lost to the universe, and heat energy is disordered, the entropy of the universe is increasing. This is called the **second law of thermodynamics**.





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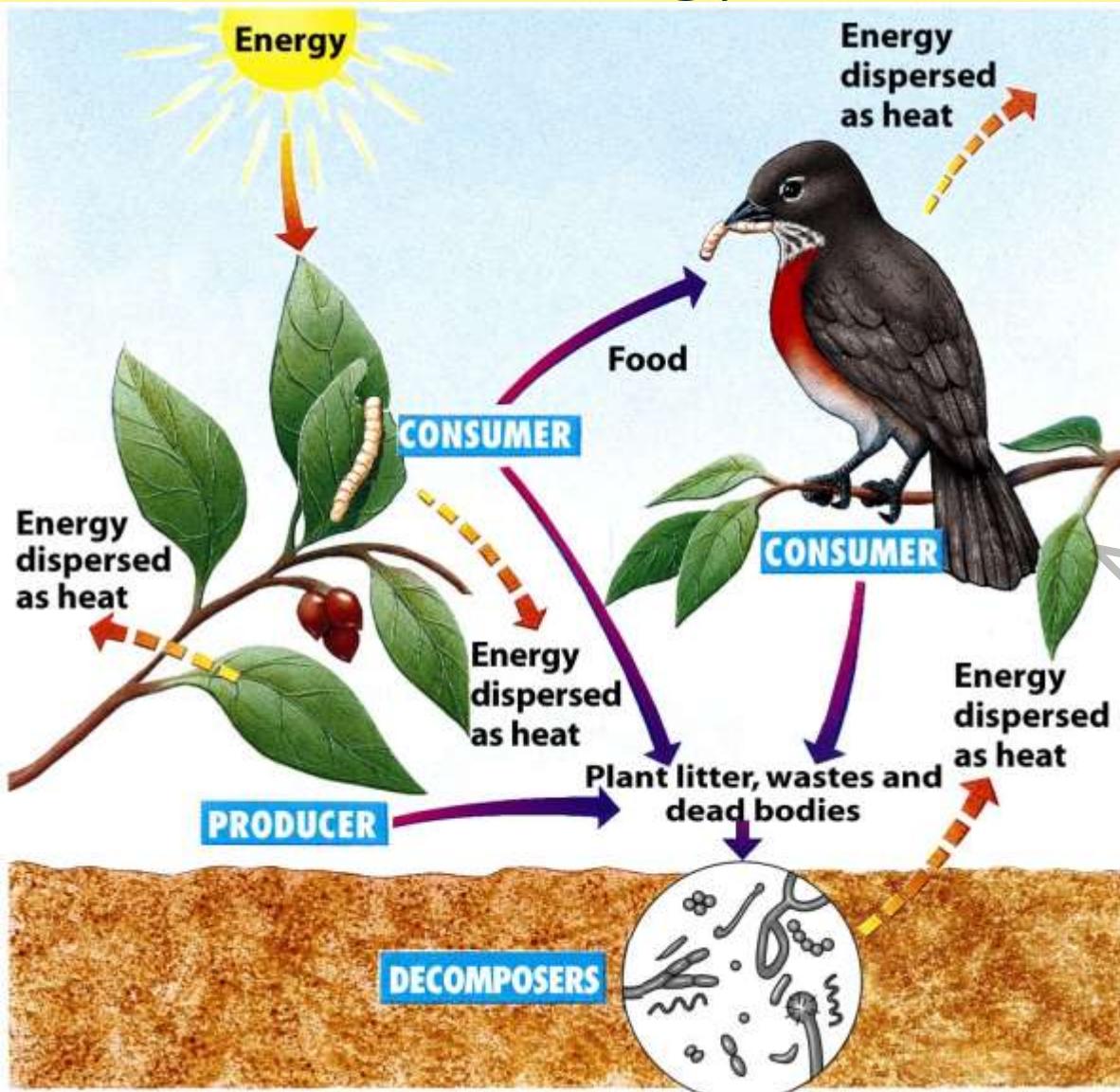
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Week-3 Topics

Ecology, Population & Environmental Chemistry
Lecture 12 : Energy Flow and Ecological Concepts

The Flow of Energy



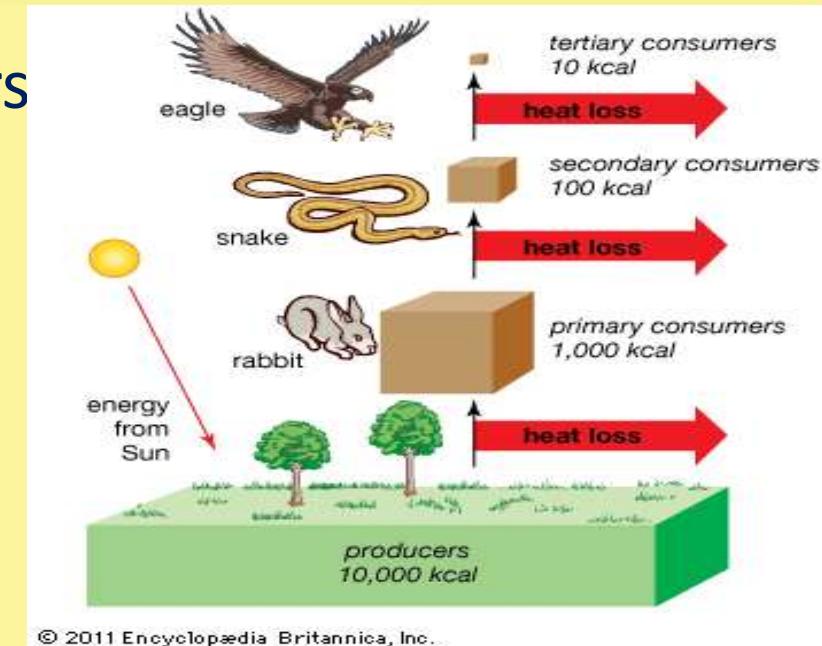
From Producers



To Consumers



And finally to
Decomposers



Producers:

Also called autotrophs

Use light or chemical energy to make food

- 1. Plants**
- 2. plant-like protists (algae)**
- 3. Bacteria**



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Heterotrophs

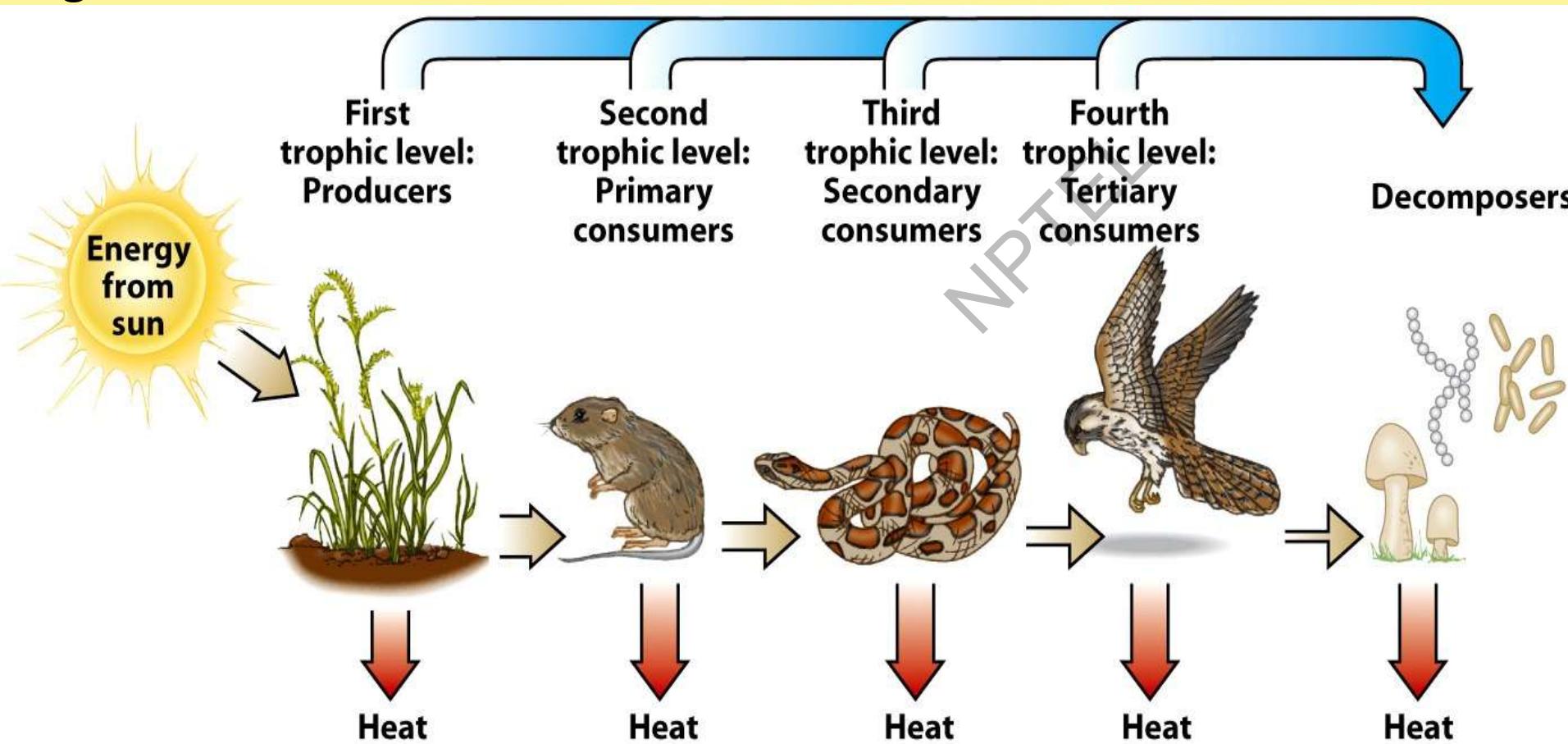
- Organisms that rely on other organisms for their energy and food supply
- Also called heterotrophs
- Heterotrophs (=other-nourishing) cannot produce their own food directly from sunlight+ inorganic compounds. They require energy previously stored in complex molecules.
- Heterotrophs can be grouped as: consumers decomposers

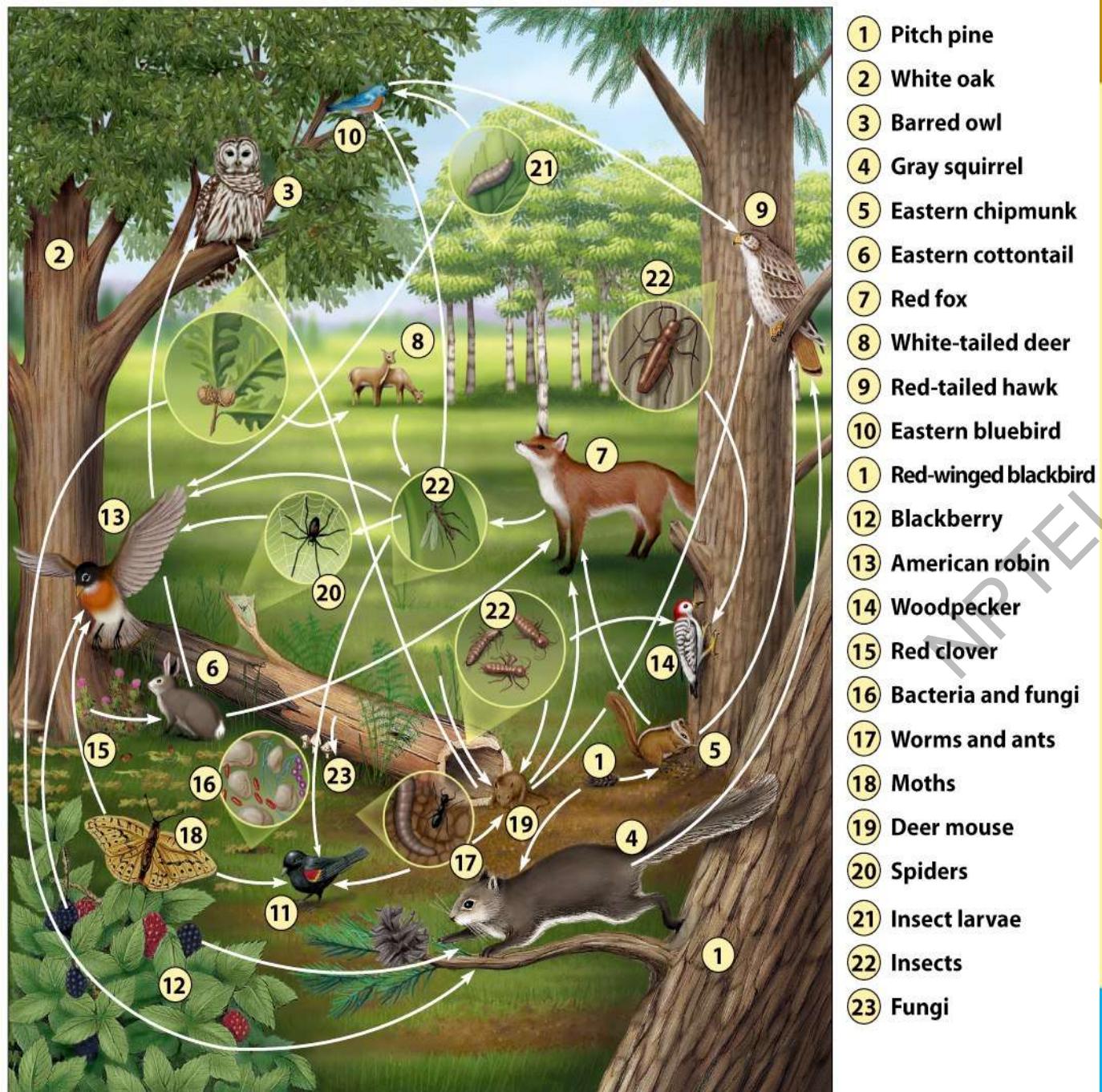


The Path of Energy Flow

Food Chains –

Shows the flow of energy in an ecosystem where energy from food passes from one organism to another





The Path of Energy Flow

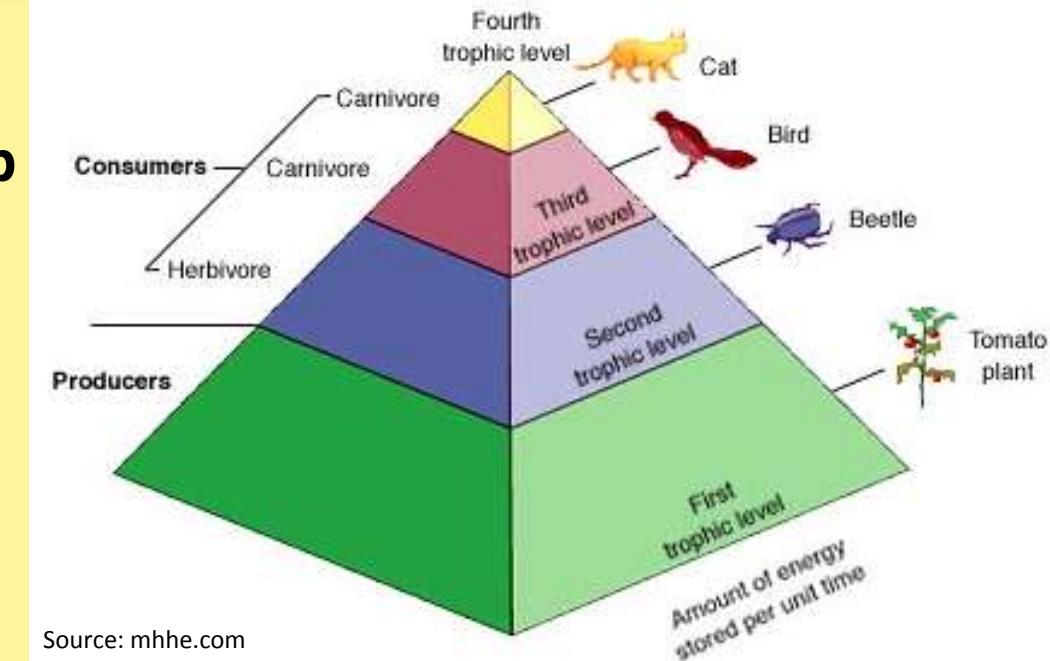
Food Webs

- Consist of interlocking food chains
- Takes into account different food sources for an organism

Trophic Levels

Trophic Levels—each step in a food chain or food web

1. Level 1—Producers (autotrophs)
2. Level 2—Primary Consumers (herbivores)
3. Level 3—Secondary Consumers
(carnivores or omnivores)
4. Level 4—Tertiary Consumers
(carnivore—usually top carnivore)



Source: mhhe.com



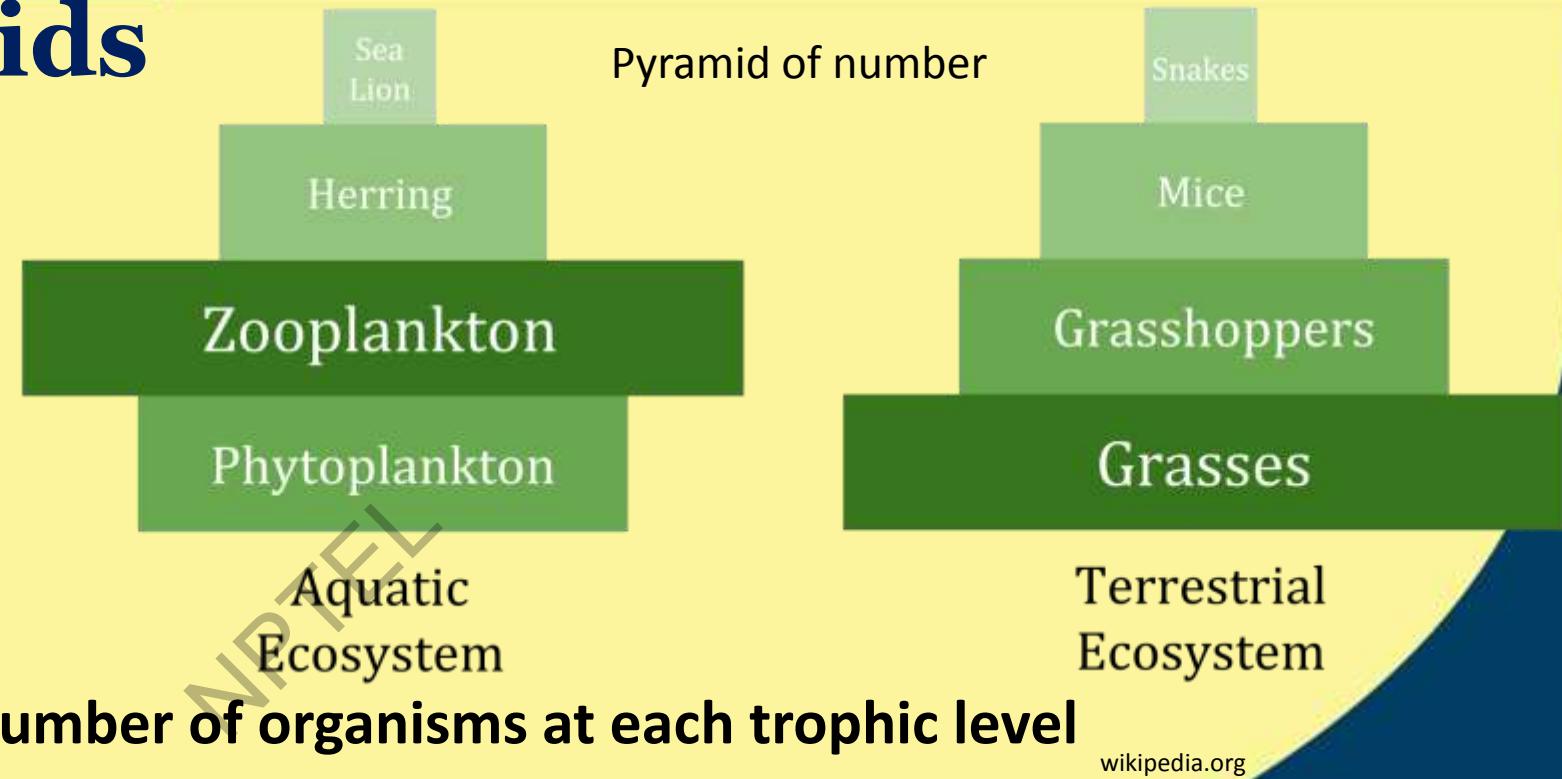
Ecological Pyramids

It graphically represent the relative energy values of each trophic level.

1. **Pyramid of number**
2. **Pyramid of biomass**
3. **Pyramid of Energy**

•A pyramid of numbers shows the number of organisms at each trophic level in a given ecosystem

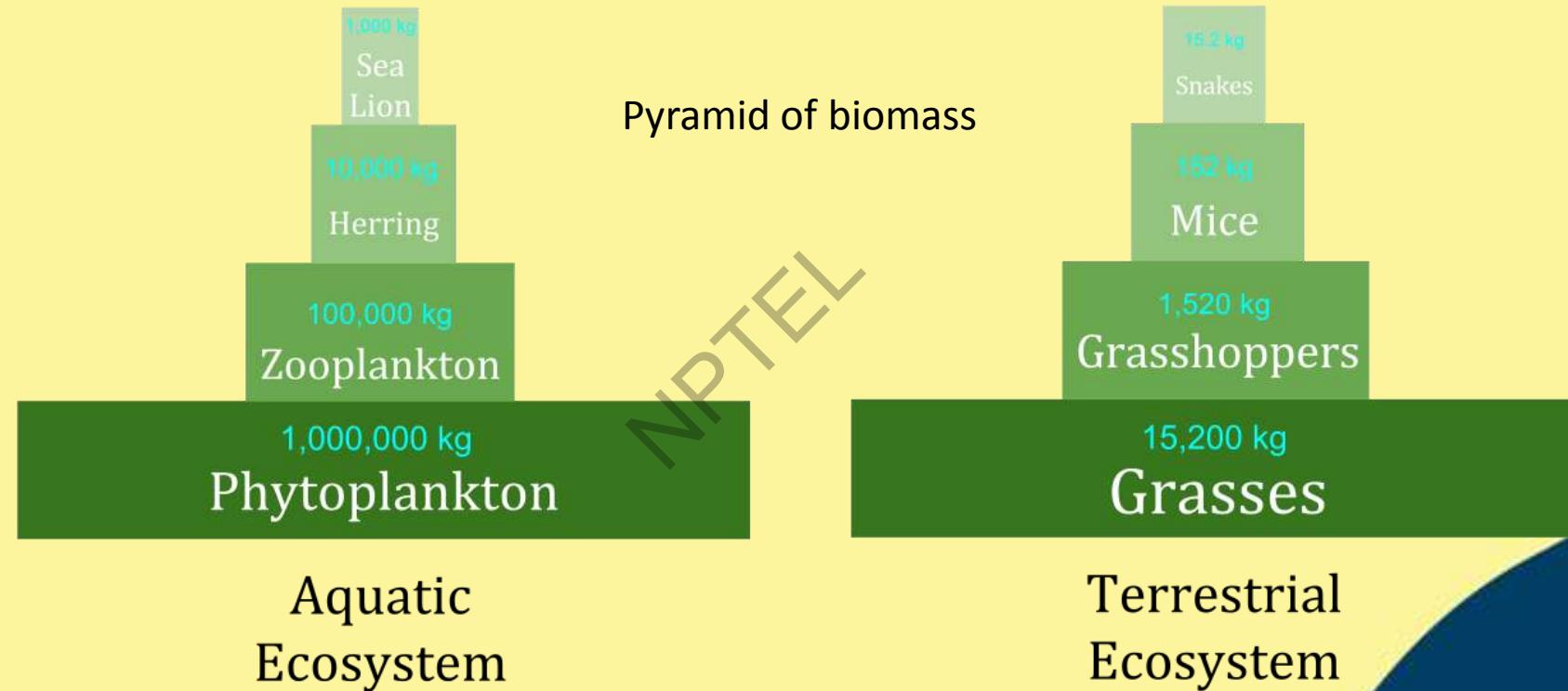
•A "pyramid of numbers" shows graphically the population of each level in a food chain. It is an upright pyramid given in an ecosystem, where usually the producers are more in number than any other Trophic level.



wikipedia.org

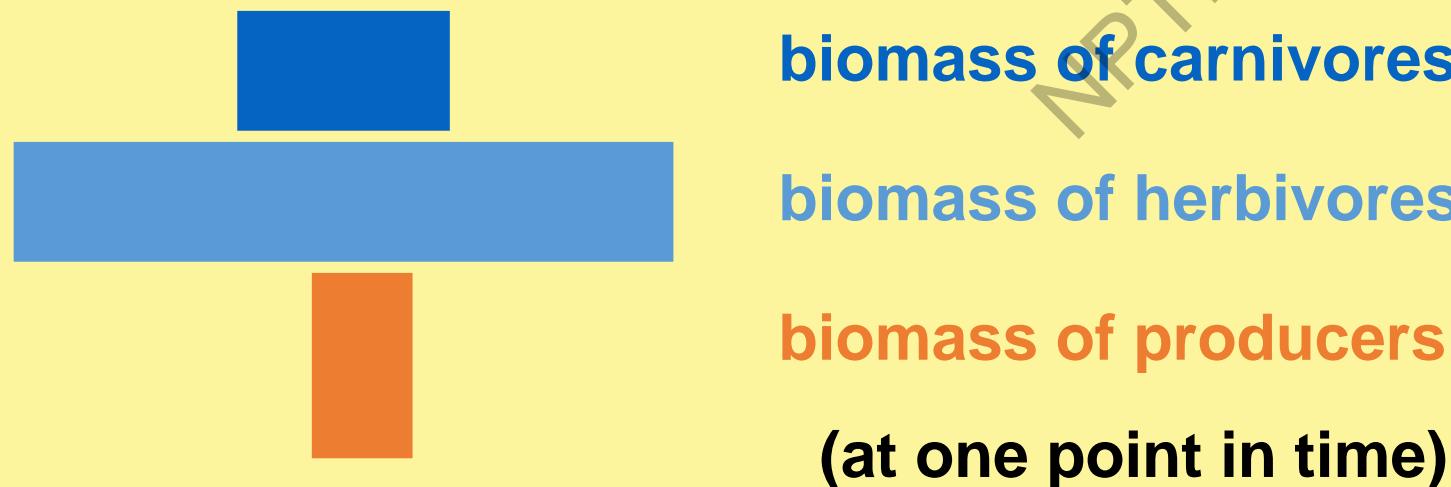


A "pyramid of biomass" shows the relationship between biomass and trophic level by quantifying the biomass present at each trophic level of an energy community at a particular time.

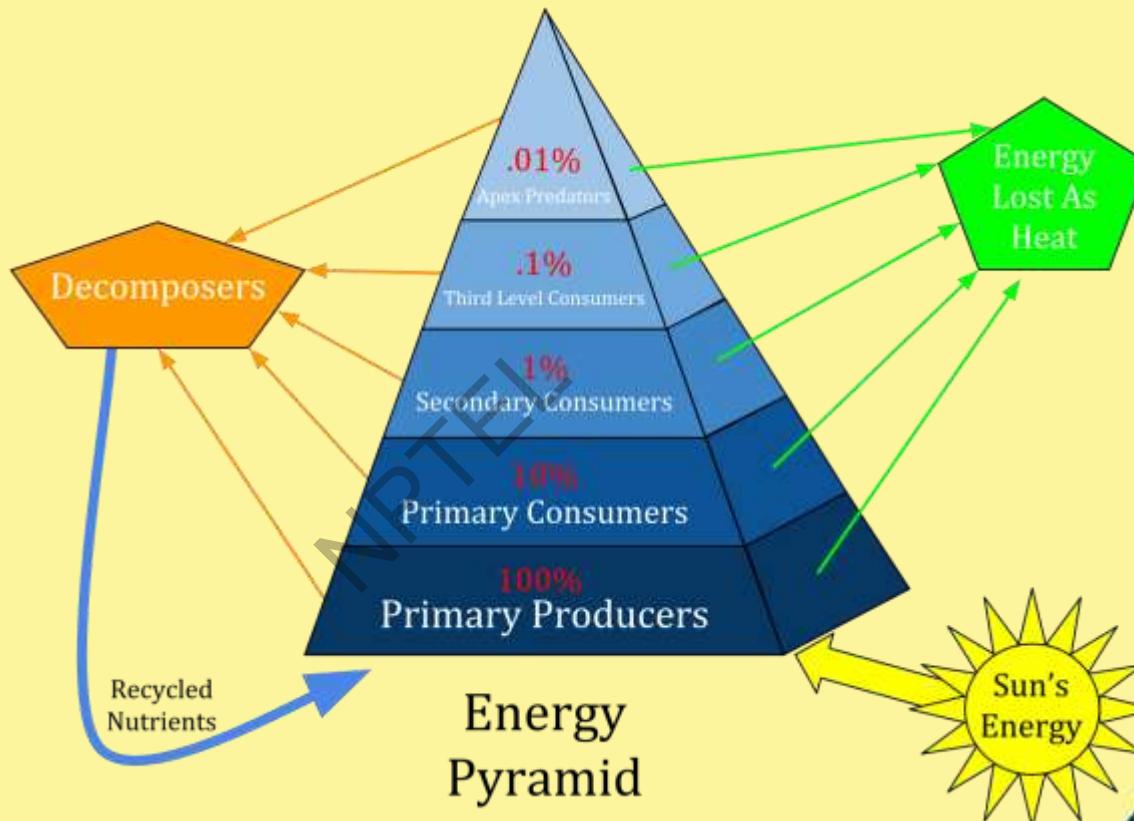


Inverted pyramids

- A pyramid of standing crop (or of numbers) may be inverted, i.e., a higher trophic level may have a larger standing crop than a lower trophic level.
- This can occur if the lower trophic level has a high rate of turnover of small individuals (and high rate of productivity), such that the First and Second Laws of Thermodynamics are not violated.



A "pyramid of productivity" is often more useful, showing the production or turnover (the rate at which energy or mass is transferred from one trophic level to the next) of biomass at each trophic level.



wikipedia.org



Biomagnification

DDT concentration:
increase of
10 million times

DDT in
fish-eating birds
25 ppm

DDT in
large fish
2 ppm

DDT in
small fish
0.5 ppm

DDT in
zooplankton
0.04 ppm

DDT in water
0.000003 ppm



Heavy metals

Ex: mercury

Pesticides

Ex: DDT

(dichlorodiphenyltrichloroethane)

Organochlorides:

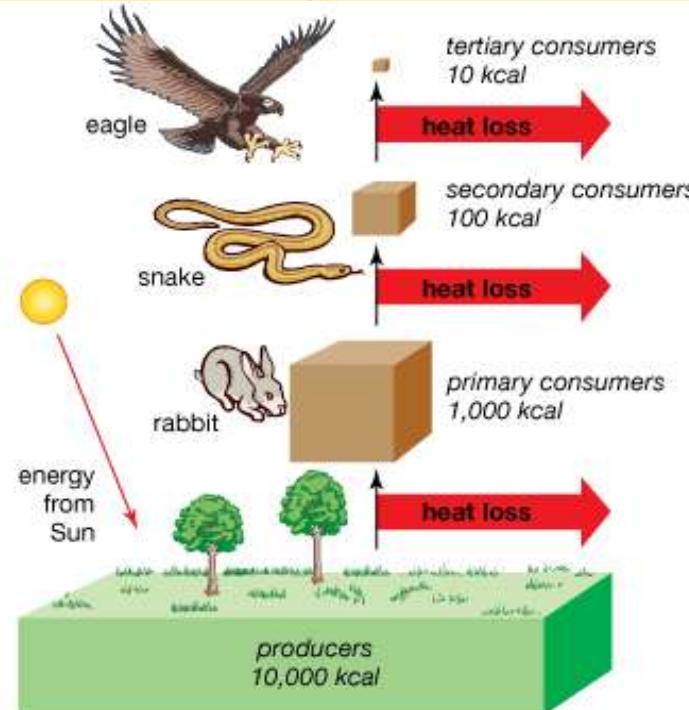
Ex: PCBs

Ecological efficiency

- Ecological efficiency describes the efficiency with which energy is transferred from one trophic level to the next. It is determined by a combination of efficiencies relating to organismic resource acquisition and assimilation in an ecosystem.

What is 10% rule?

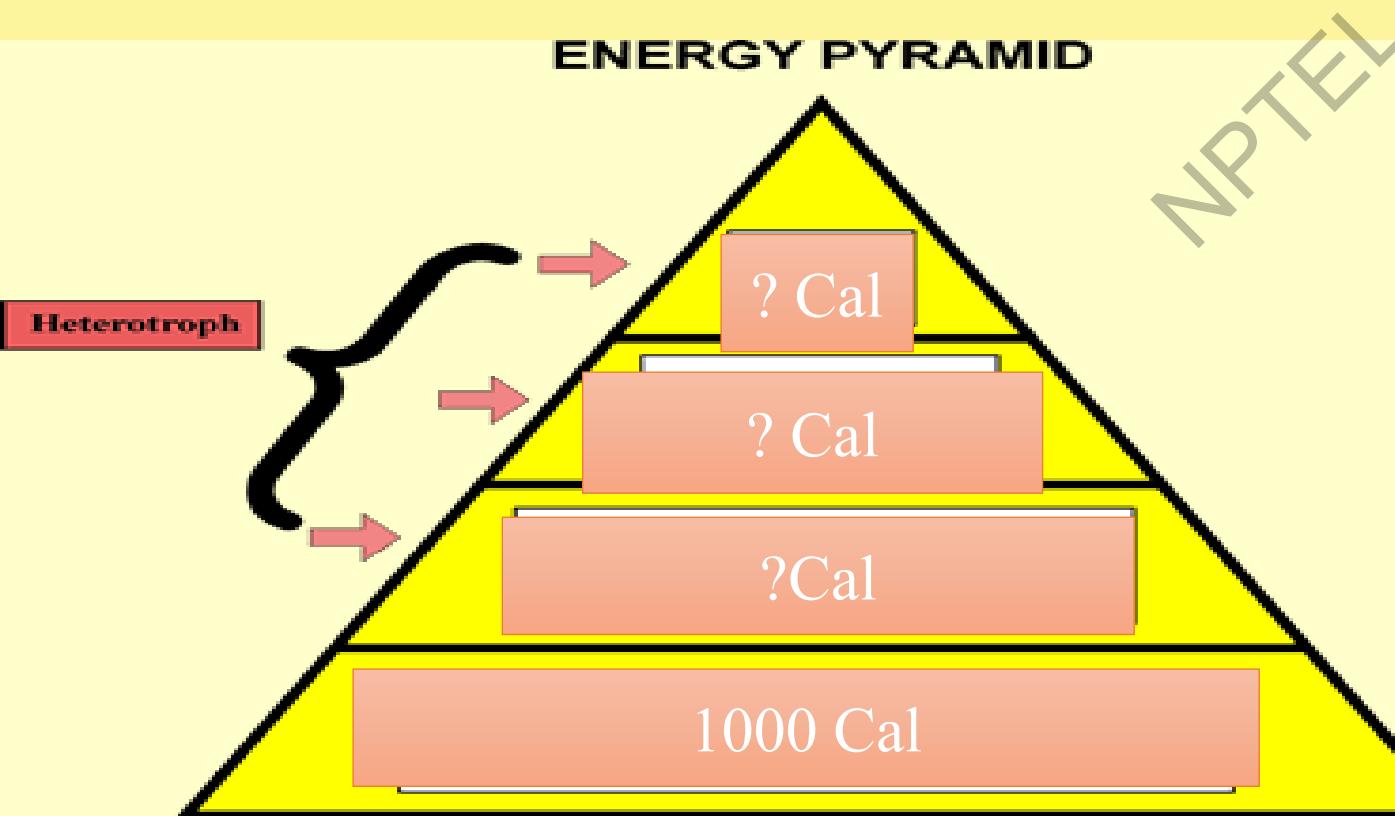
An average of only 10% of the energy in one trophic level is passed to the next trophic level.



Why do you think only 10% of the total energy from 1 trophic level is passed to the next?

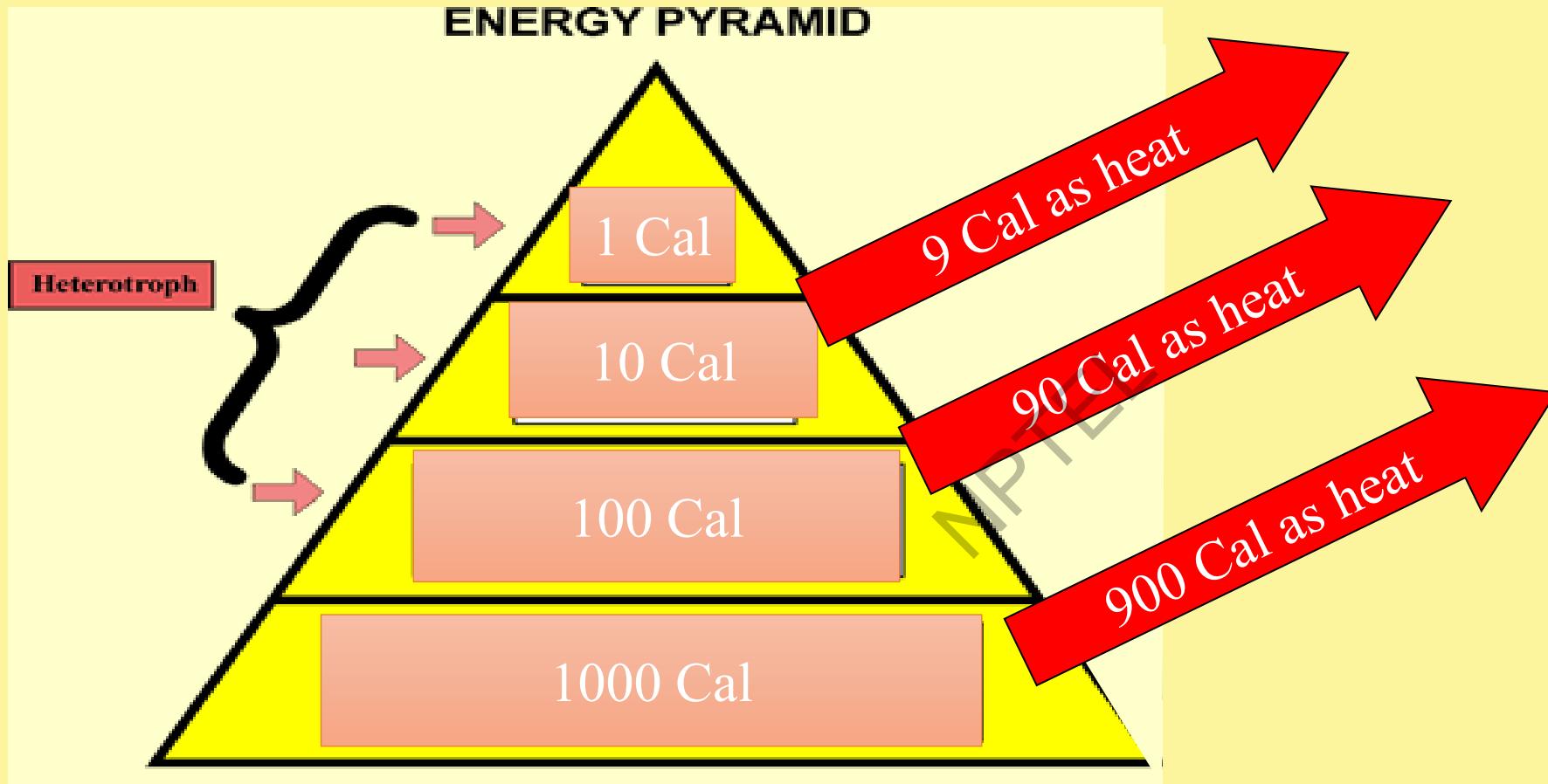
Reasons for decrease in available energy

1. Energy is “used up” for daily life activities.
2. Not all organisms that die are eaten by animals in the next trophic level.
3. Not all parts of an organism are eaten and digested for energy.



How much energy is at each level?

Answer



The rules of ecology- by Barry Commoner

1. Everything is connected to everything else.
2. Everything must go somewhere.
3. Nature knows best
4. There is no such thing as a free lunch.

To understand any system you must understand the next larger system.

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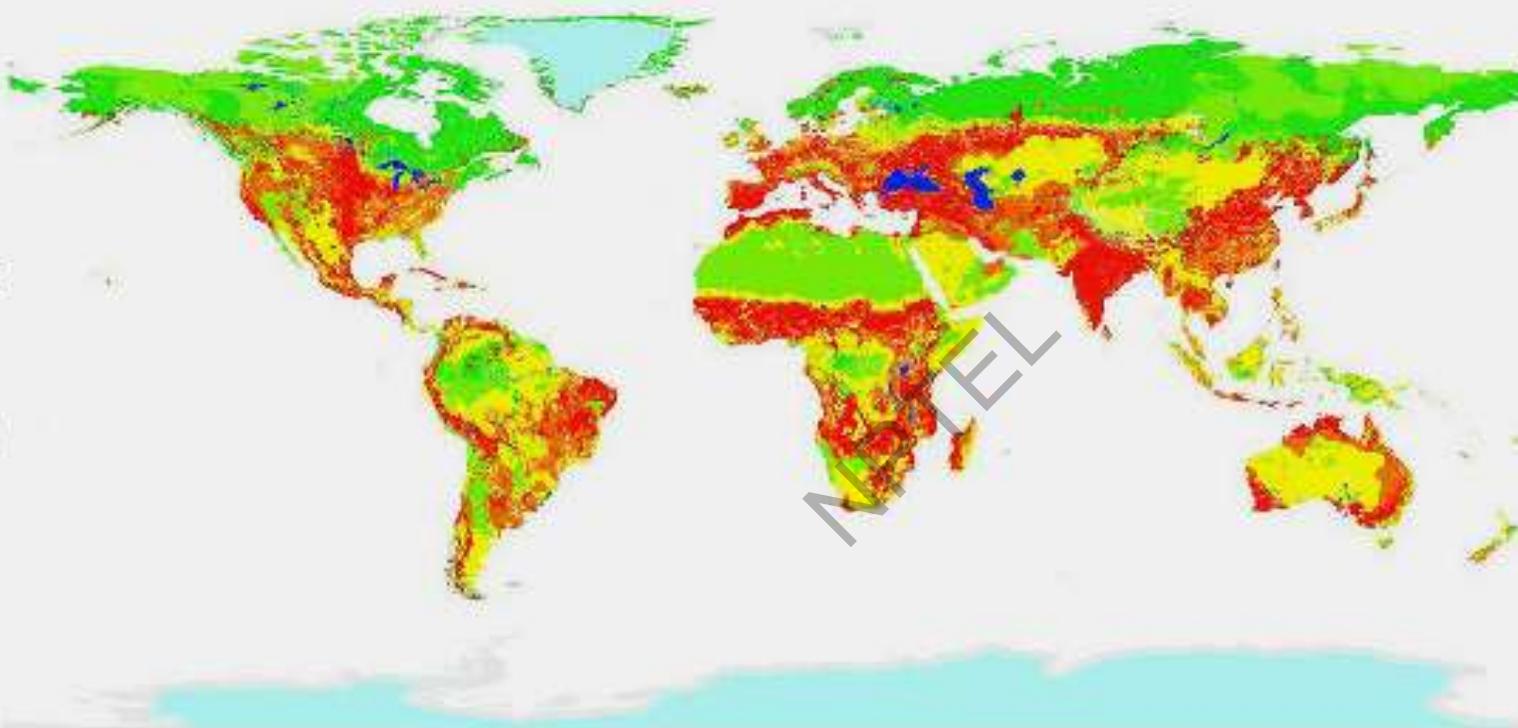


Blue planet under threat

The map is shaded according to **risk index** which indicates threats from loss of above-ground diversity, pollution, nutrient over-loading, over-grazing, intensive agriculture, fire, soil erosion, desertification & climate change

Risk index

| | |
|--|-----------|
| | VERY LOW |
| | LOW |
| | MODERATE |
| | HIGH |
| | VERY HIGH |
| | WATER |
| | ICE |



90% of the world's seabirds may have bits of plastic in their stomachs

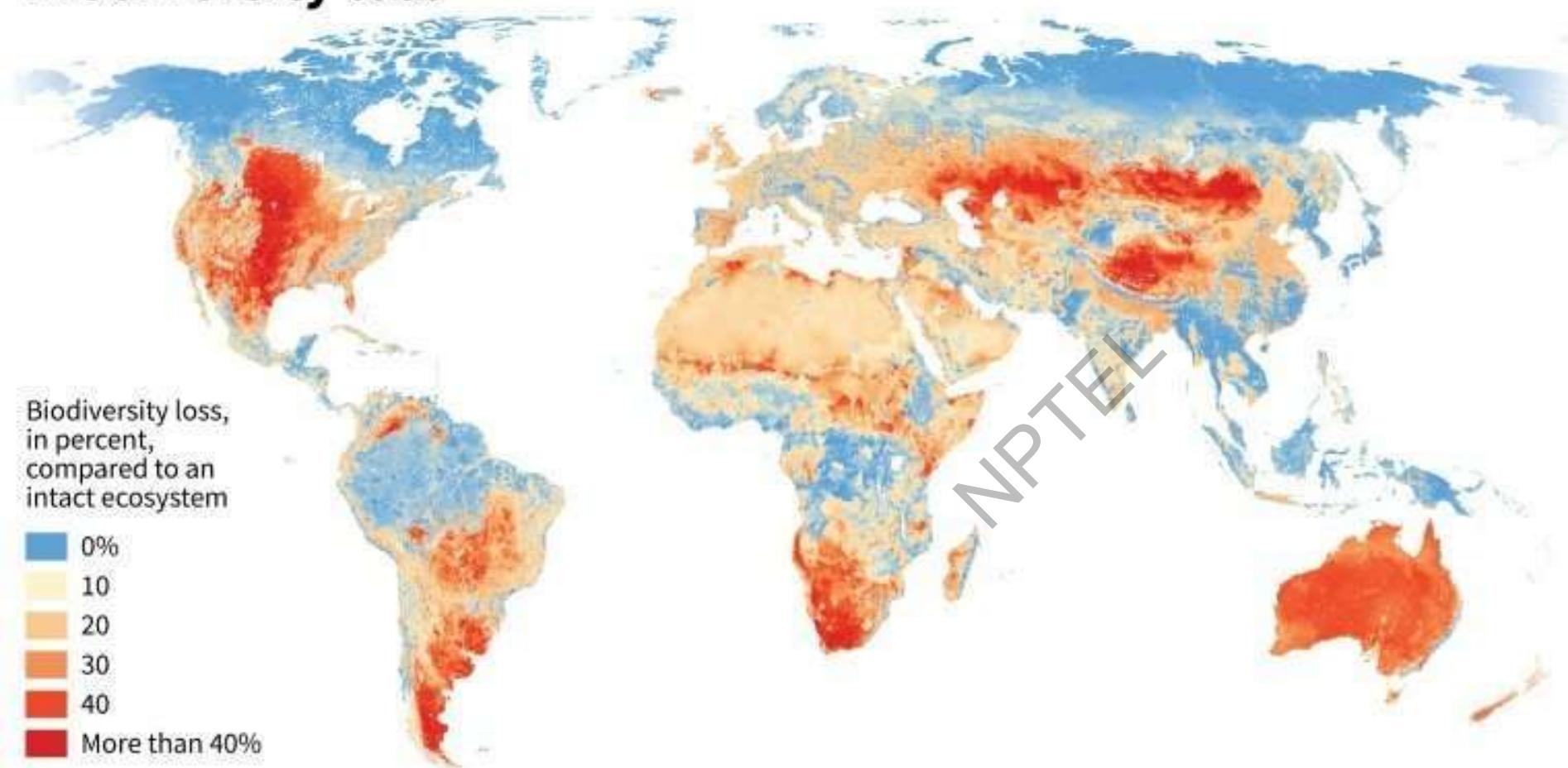
20% of the Amazon rainforest has disappeared in the last 50 years

170 The number of times global temperature has risen

60% The fall in the numbers of fish, birds, mammals and reptiles from 1970 to 2014 (WWF)



Biodiversity loss



Biodiversity loss,
in percent,
compared to an
intact ecosystem

- 0%
- 10
- 20
- 30
- 40
- More than 40%

Source: National History Museum Data Portal. Data from 2016

© AFP





Habitat change—deforestation, urbanization, conversion to farmland—emerged as the biggest cause of insect decline and extinction threat.

<https://phys.org/news/2019-02-world-catastrophic-collapse-insects.html>





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Lecture 13 : Population

Population

Population forecasting methods:

The following are the standard methods by which the forecasting population is done.

- i. Arithmetical increase method
- ii. Geometrical increase method
- iii. Incremental increase method
- iv. Simple graph method
- v. Decrease rate of growth method
- vi. Comparative graph method and The master plan method

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Example:

Problem: The following data have been noted from the census department for a city A . Find the probable population in the year 1980, 1990 and 2000.

| YEAR | POPULATION |
|------|------------|
| 1940 | 8000 |
| 1950 | 12000 |
| 1960 | 17000 |
| 1970 | 22500 |



Arithematical increase method

This method is based on the assumption that the population is increasing at a constant rate. The rate of change of population with time is constant.

The population after „n“ decades can be determined by the formula.

$$P_n = P + n.c$$

where $P \rightarrow$ population at present $n \rightarrow$ No. of decades $c \rightarrow$ Constant determined by the average of increase of „n“ decades

| Year | Population | Increase in population |
|------|------------|------------------------|
| 1940 | 8000 | |
| 1950 | 12000 | 4000 |
| 1960 | 17000 | 5000 |
| 1970 | 22500 | Average = 4833 |



| Year | Population |
|------|------------|
|------|------------|

| | |
|------|----------------------------|
| 1980 | $22500 + 1 * 4833 = 27333$ |
|------|----------------------------|

| | |
|------|----------------------------|
| 1990 | $22500 + 2 * 4833 = 32166$ |
|------|----------------------------|

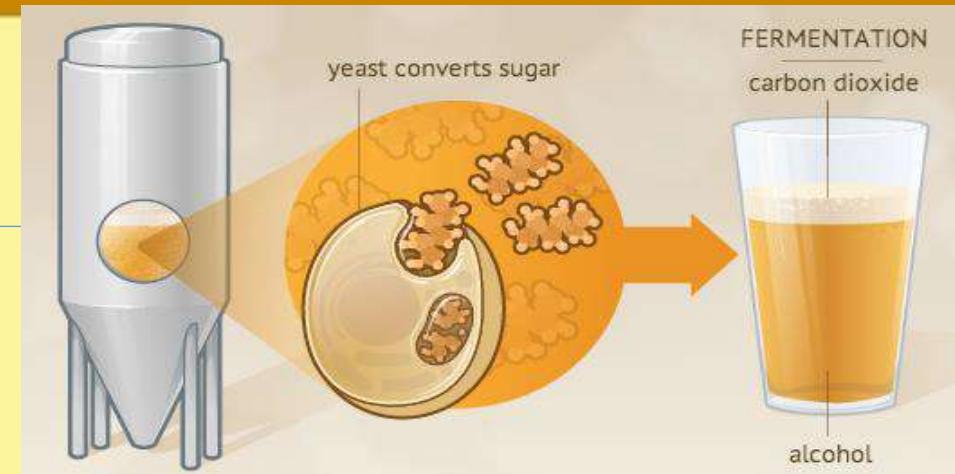
| | |
|------|----------------------------|
| 2000 | $22500 + 3 * 4833 = 36999$ |
|------|----------------------------|

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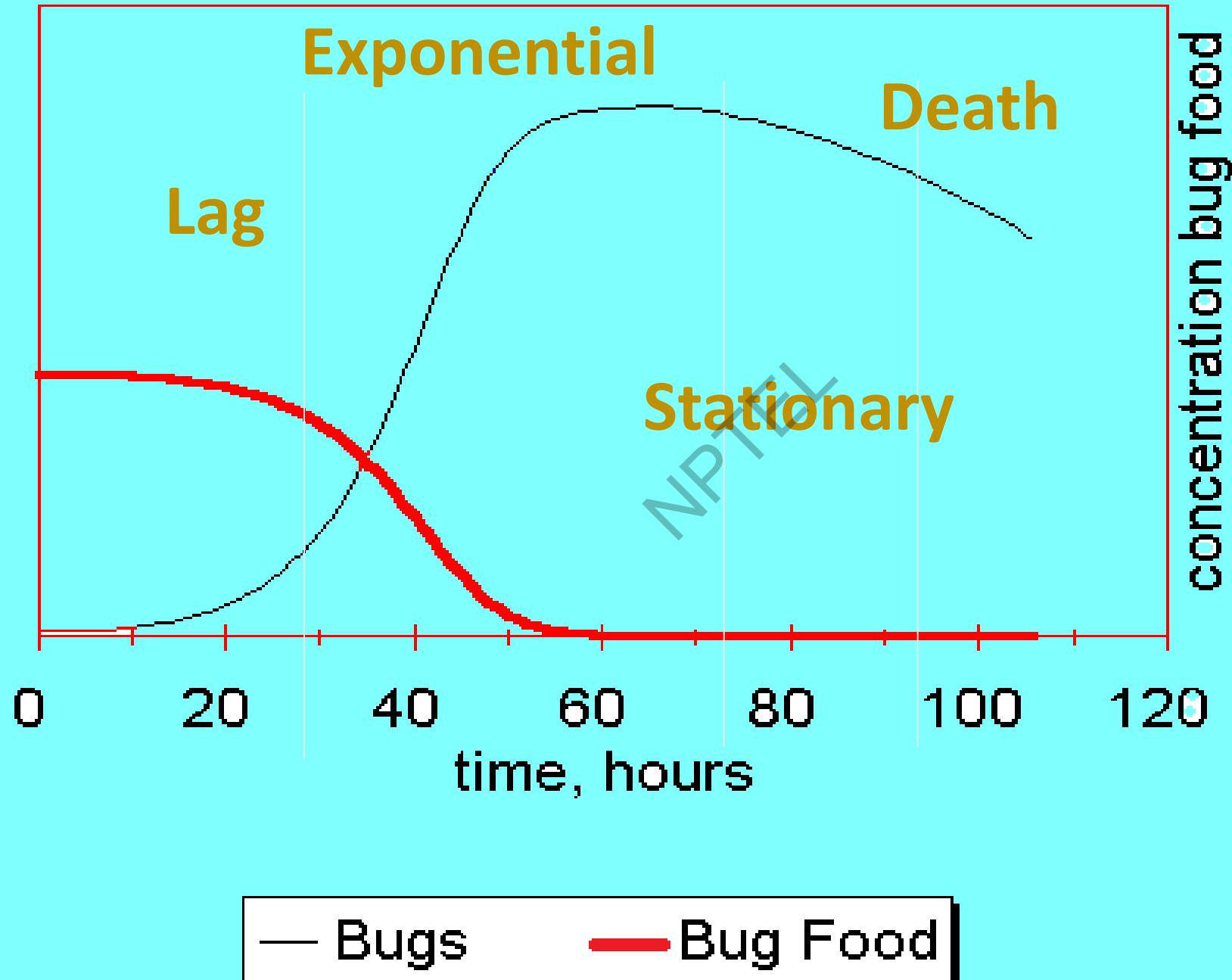


Population Growth

- Just like making BEER!
- Population growth modelling follows the same exponential trend as yeast growth during fermentation.
- Beer = Yeast + malt/sugar + hops
- Sugar acts as food for the yeast
- Yeast consumes the sugar, multiplies and produces alcohol and flavours as a waste product
- Population = Environment + People + Resources



bug cell numbers



Animal and Human Populations

- Growth is also exponential
- $P = P_0 e^{rt}$
- P = future size of population
- P_0 = current size of population
- t = number of years
- r = assumed constant growth rate

The rate is often expressed as a percentage (e.g. NZ's current population growth rate is 1.4%)



Growth Rate

Determined by four principle components

$$r = (b-d) + (i-e)$$

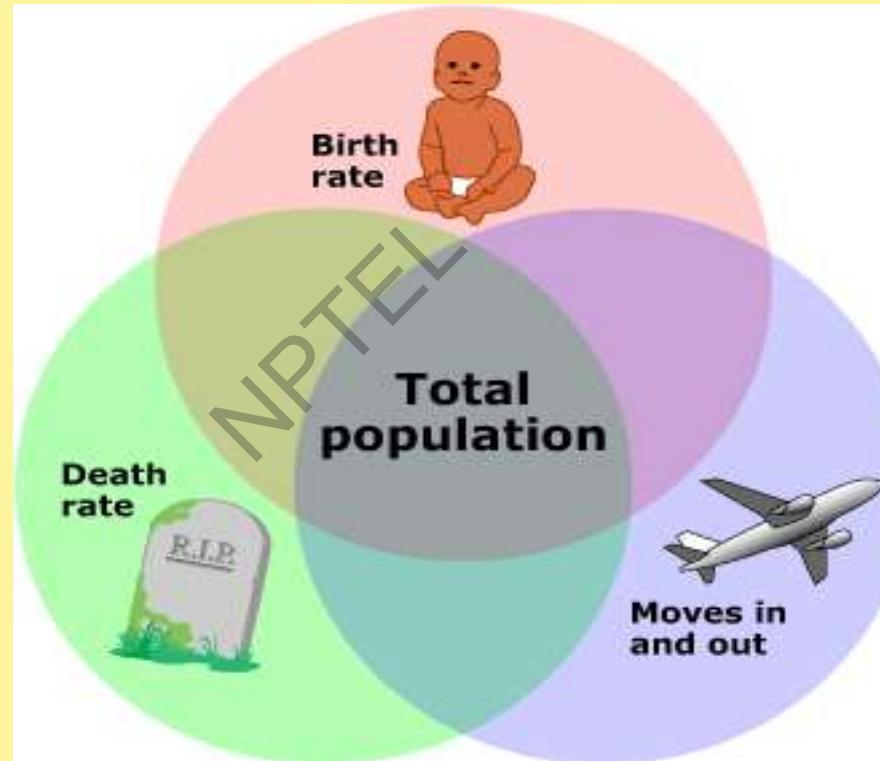
Where

b = birth rate

d = death rate

i = immigration rate

e = emigration rate



Factors Affecting Birth Rate

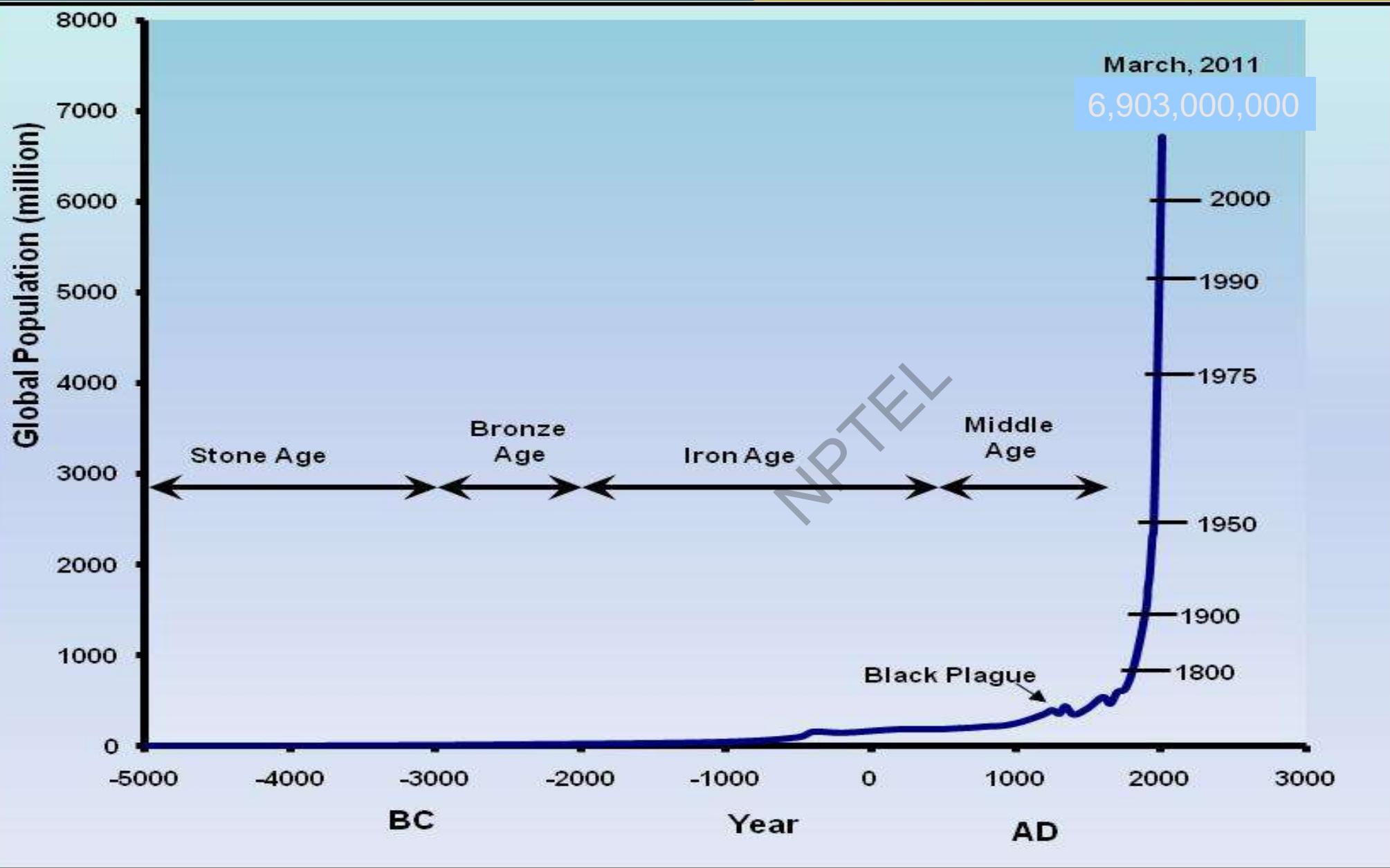
- Number of children
- Age of bearing children
- Infant mortality
- Health of population
- General age of population
- Age of death vs period of fertility
- Education level of population



Factors Affecting Death Rate

- Natural life span
- Availability of health care
- Care provided to elderly
- Occupational risks
- Social stability
- Dietary factors
- Lifestyle – e.g. smoking





World population 0 AD to 2100
One point equals 1 million people

Population: 170 Million



World population 0 AD to 2100

One point equals 1 million people

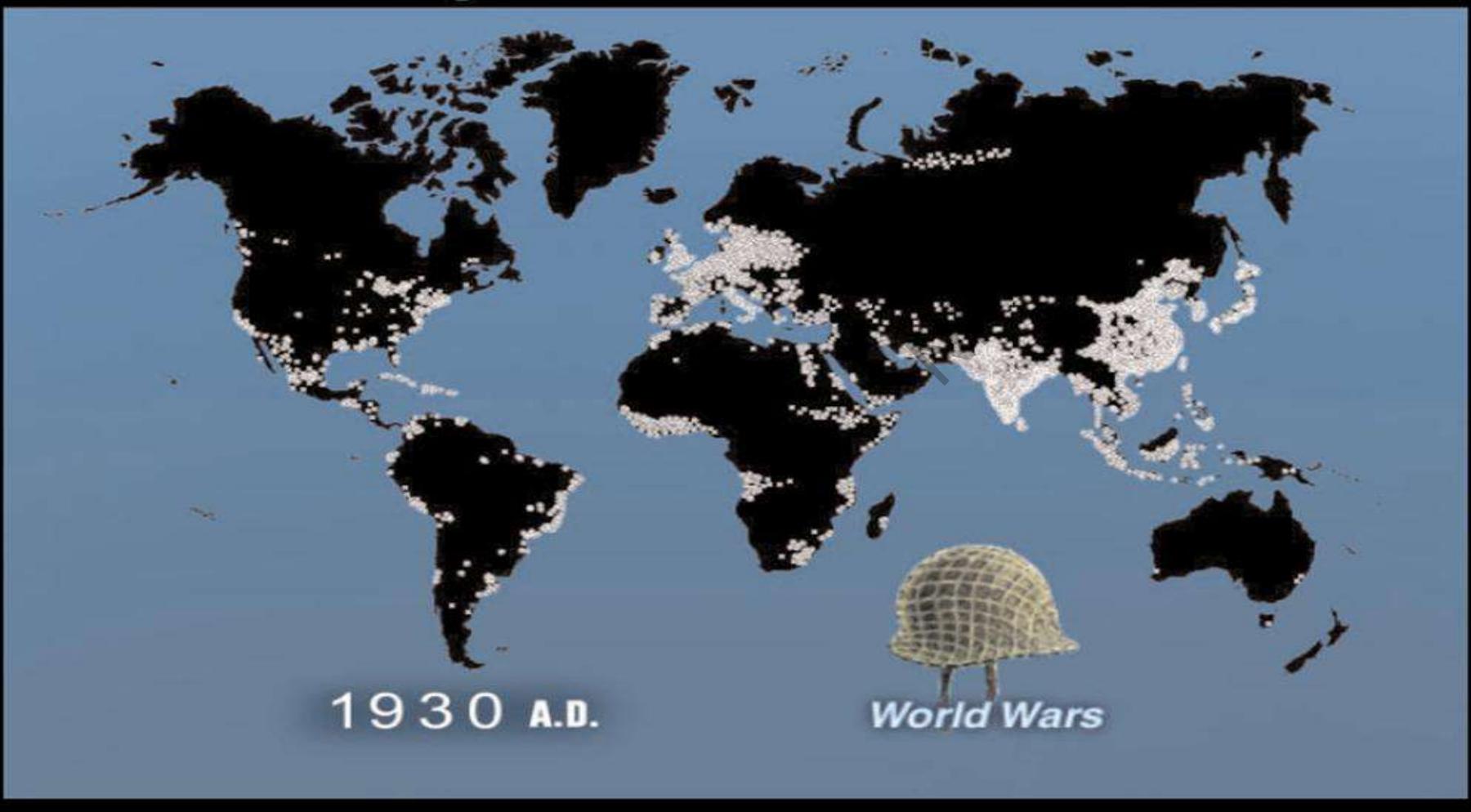
Population: 1 Billion



World population 0 AD to 2100

One point equals 1 million people

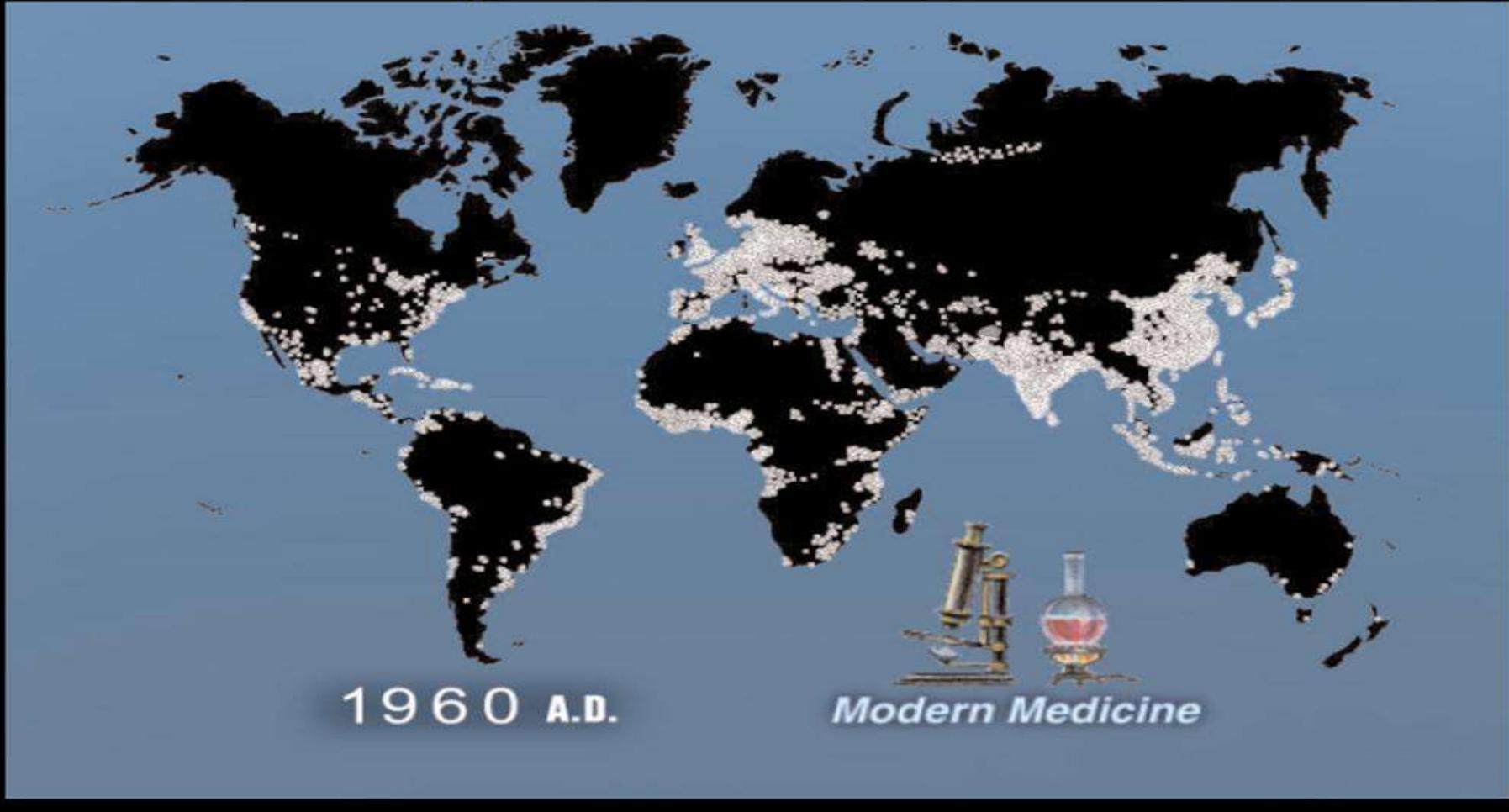
Population: 2 Billion



World population 0 AD to 2100

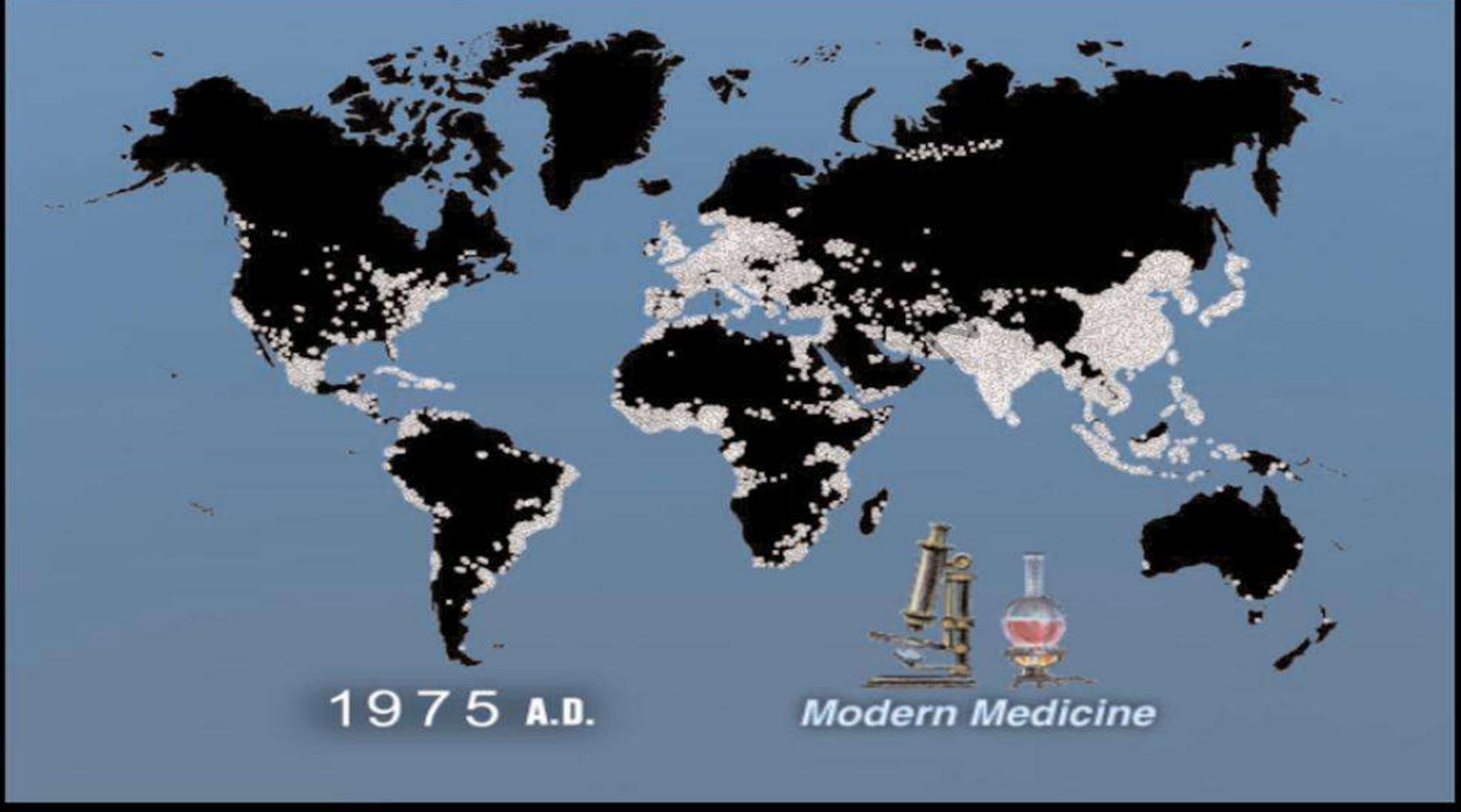
One point equals 1 million people

Population: 3 Billion



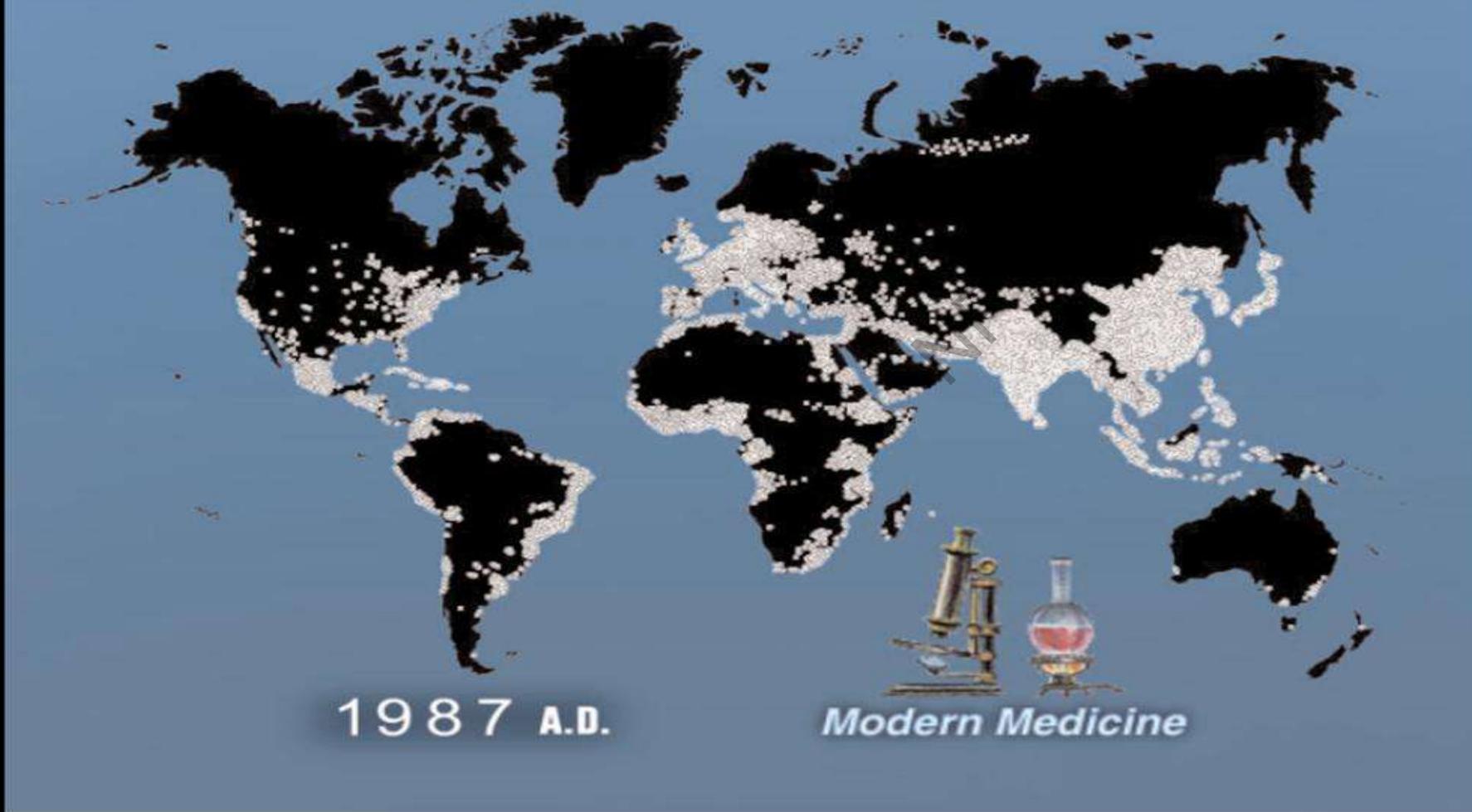
World population 0 AD to 2100
One point equals 1 million people

Population: 4 Billion



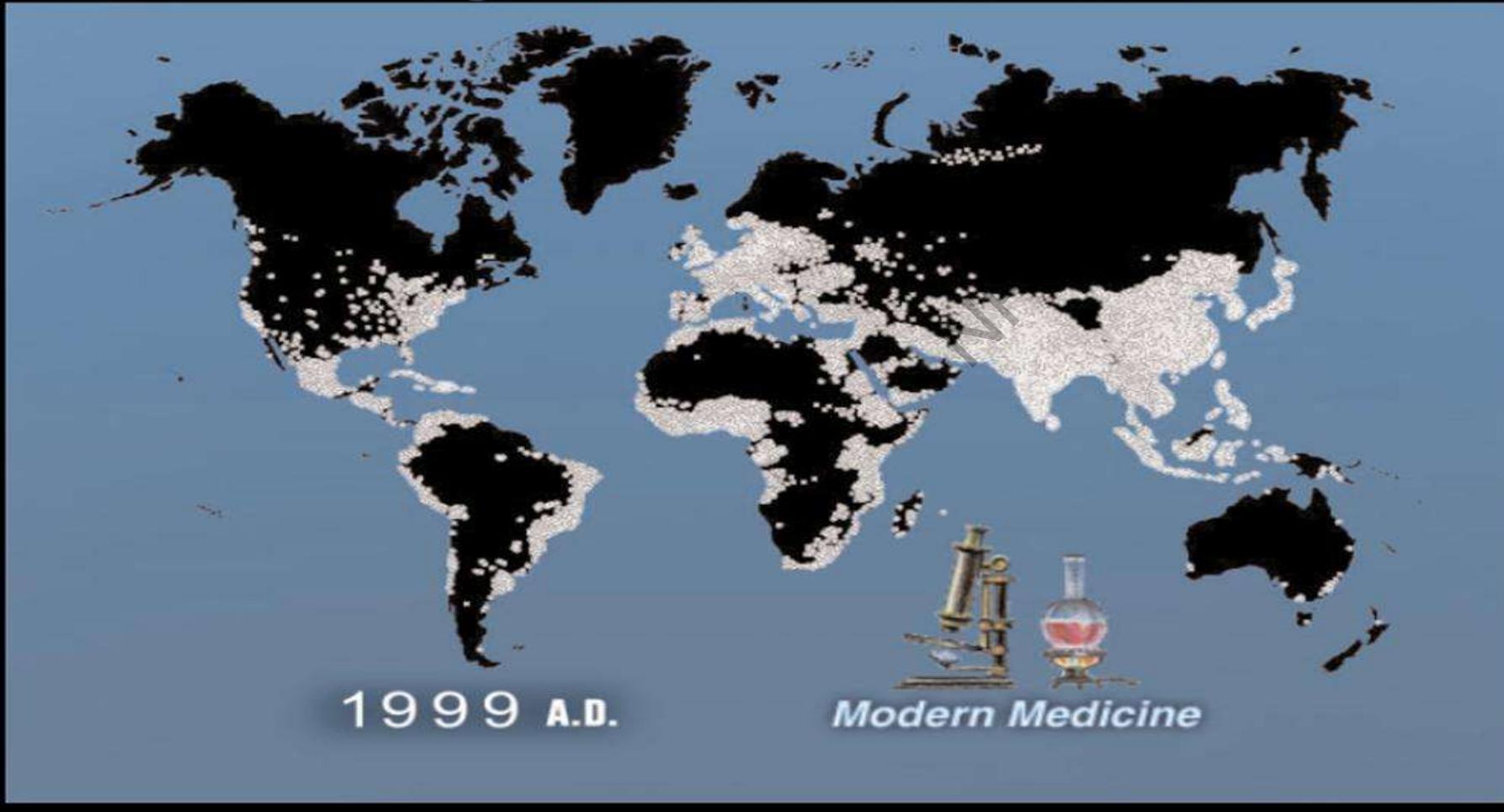
World population 0 AD to 2100
One point equals 1 million people

Population: 5 Billion



World population 0 AD to 2100
One point equals 1 million people

Population: 6 Billion



World population 0 AD to 2100

One point equals 1 million people

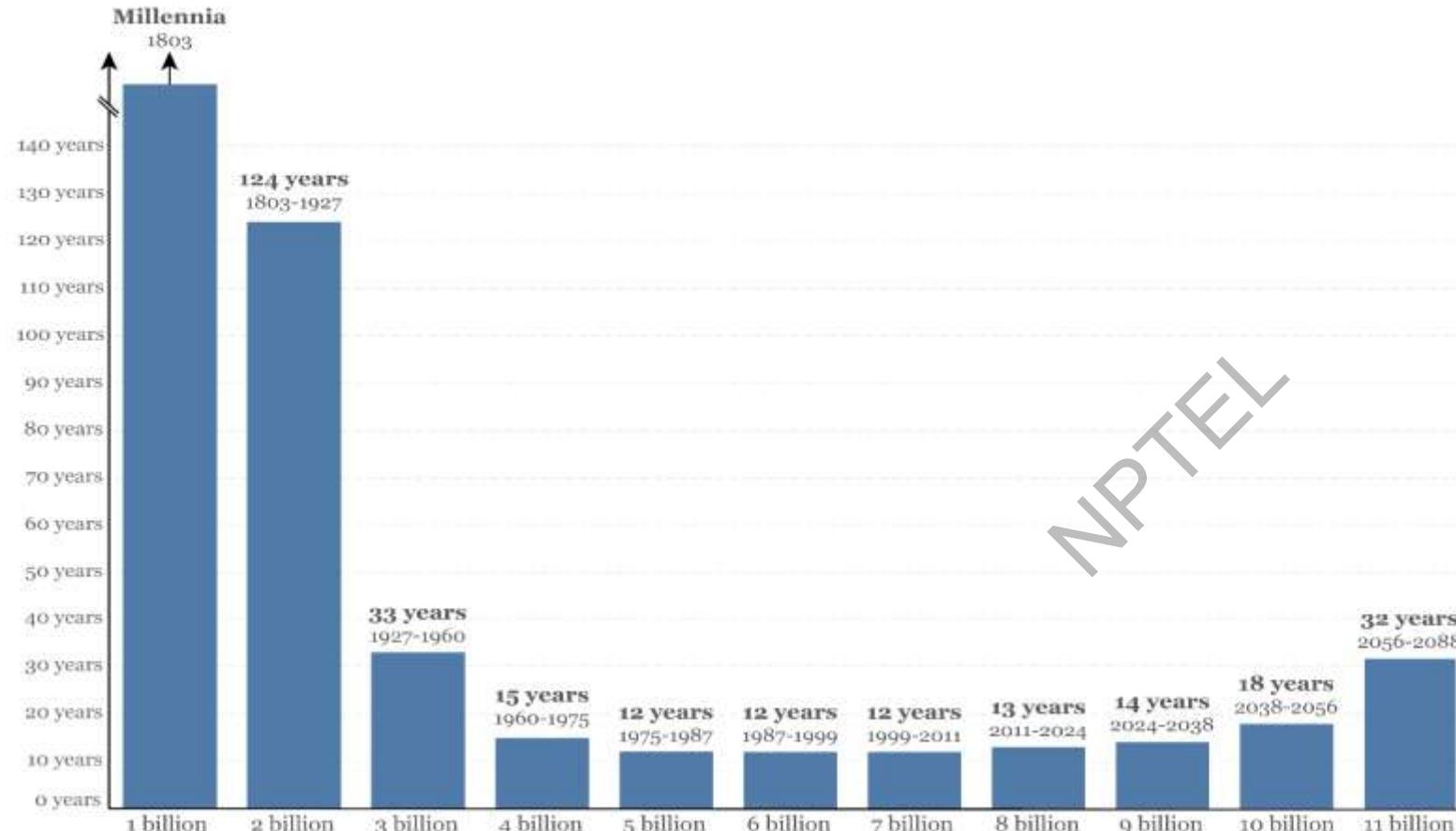
Est. Population: 8 Billion



Time for global population to increase by one billion

The number of years taken for the global population to increase by one billion. Also shown are the years over which this billion was added. Figures from 7 billion onwards are based on the UN's medium projection to 2100.

OurWorld
in Data



Data source: History Database of the Global Environment (HYDE); UN World Population Prospects (2015 Revision); UN Medium Projection (2015 Revision)

The data visualization is available at OurWorldInData.org. There you find research and more visualizations on this topic.

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**Lecture 14 : Population, Consumption &
Biodiversity**

Population growth rates

- Global growth rate for 2005–2010 was 1.2%
- At that growth rate, population will be 11.1 billion by 2050, 15 billion by 2070
- Overall, growth rate is slowing due to changes in population and social dynamics – sustainable living, affluence, education
- 2010 - 1.20%
- 2050 - 0.51%
- 2095 - 0.11%



Developed Countries (18% population)

- Growth rate constant for past 200 years
- Growth rate is approximately 1% per year
- Much of the current increase due to immigration

Less Developed Countries (82% population)

0.5% growth rate prior to 1900

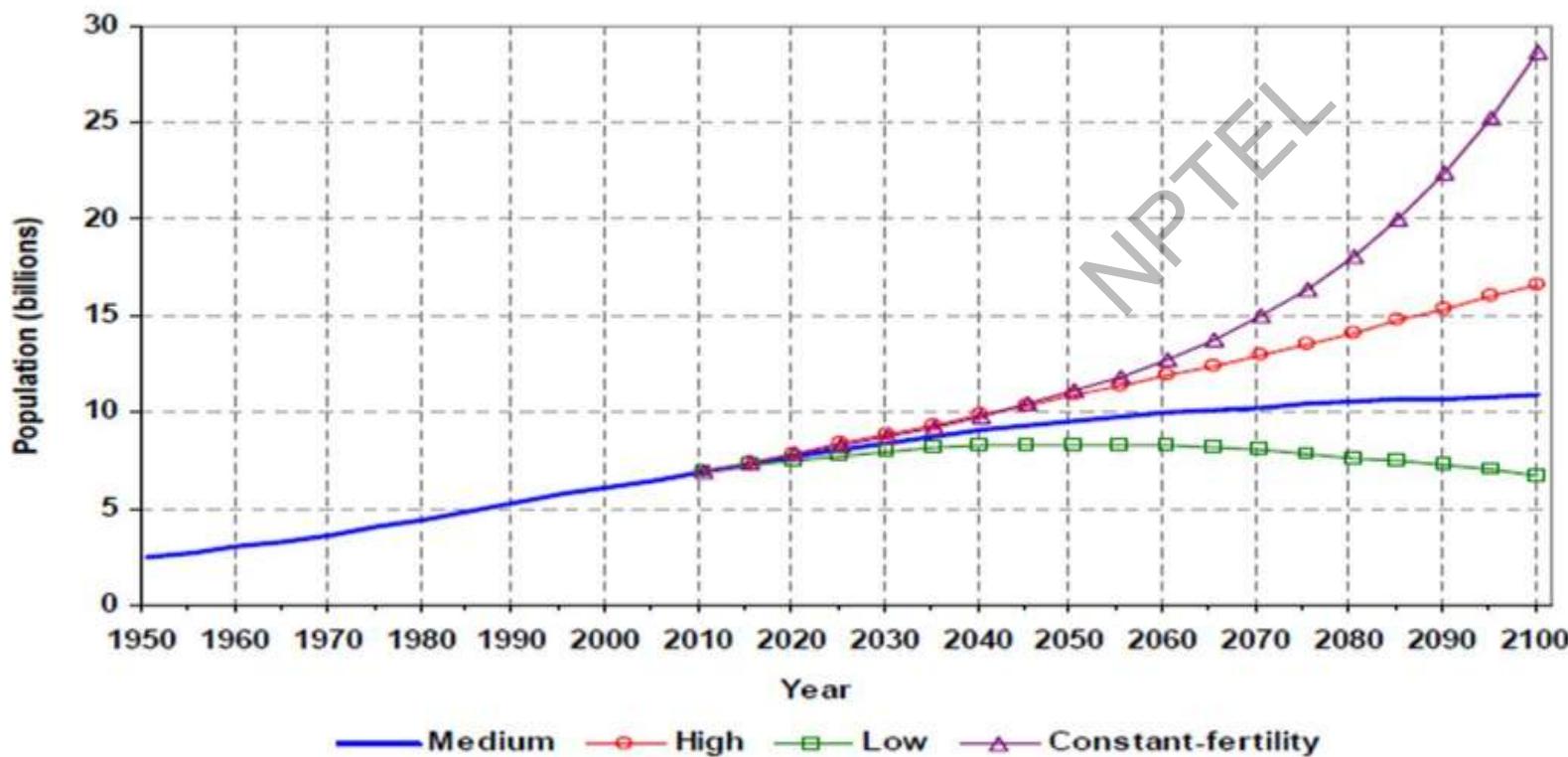
Growth rate was 2.25% per year for 1950-1980, 1.71% for 1980-2013

Rate is expected to drop in all regions except Africa



- Many competing models for population growth
- It is suspected that growth will increase into the future

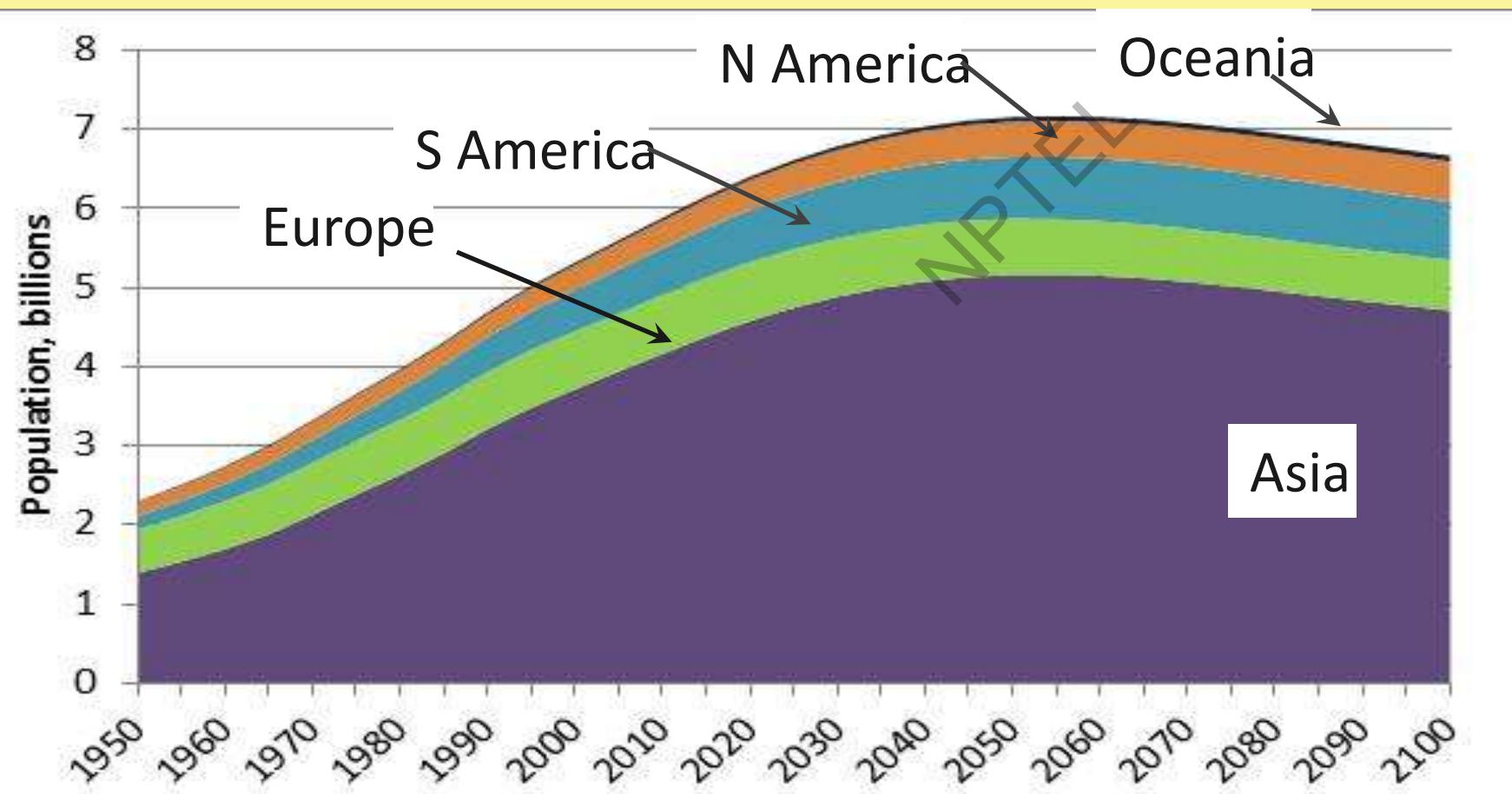
Figure 1. Population of the world, 1950-2100, according to different projections and variants



Source: Population Division of the Department of Economic and Social Affairs of the United Nations Secretariat (2013).
World Population Prospects: The 2012 Revision. New York: United Nations.

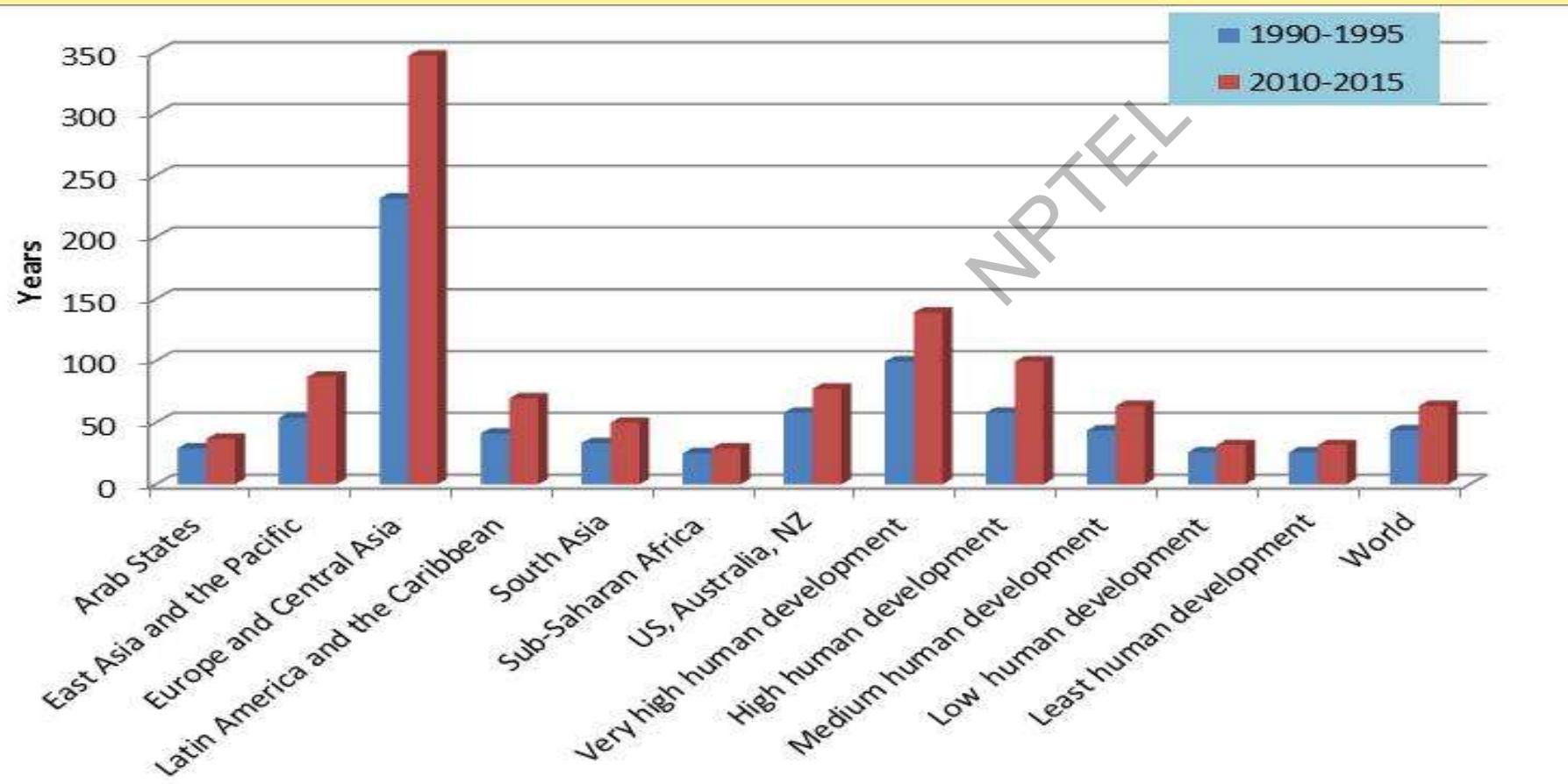
Projected population, Medium Scenario, 2013

- Population growth will decrease in all regions of the globe except Africa by 2050
- Africa is projected to account for the overall growth of the global population in the lead up to 2100 (see previous graph)



Population doubling times

Regions of lowest development show shortest time before population doubling, while medium to high development shows trend of longer time before population doubling!



Aging populations

- Median age is increasing for both developed and developing nations
- Improved Medicine, hygiene, etc -> Leads to increased overall population if birth rates remain unchanged.

TABLE I.5. MEDIAN AGE FOR THE WORLD, DEVELOPMENT GROUPS AND MAJOR AREAS,
1950, 1980, 2013, 2050 AND 2100, MEDIUM VARIANT

| Development group or major area | Median age (years) | | | | |
|---------------------------------|--------------------|------|------|------|------|
| | 1950 | 1980 | 2013 | 2050 | 2010 |
| World | 23.5 | 22.6 | 29.2 | 36.1 | 41.2 |
| More developed regions | 28.5 | 31.9 | 40.5 | 44.5 | 46.3 |
| Less developed regions | 21.4 | 20.0 | 27.2 | 34.9 | 40.6 |
| Least developed countries | 19.3 | 17.6 | 19.7 | 26.4 | 35.9 |
| Other less developed countries | 21.6 | 20.3 | 28.7 | 37.6 | 42.8 |
| Africa | 19.2 | 17.6 | 19.4 | 24.7 | 34.9 |
| Asia | 22.0 | 21.0 | 29.7 | 39.8 | 45.4 |
| Europe | 28.9 | 32.7 | 40.9 | 45.7 | 46.8 |
| Latin America and the Caribbean | 19.9 | 19.8 | 28.3 | 40.6 | 48.1 |
| Northern America | 29.8 | 30.0 | 37.7 | 40.9 | 44.6 |
| Oceania | 27.9 | 26.4 | 32.6 | 37.0 | 44.1 |

Source: Population Division of the Department of Economic and Social Affairs of the United Nations Secretariat (2013).
World Population Prospects: The 2012 Revision. New York: United Nations.
NOTE: Only countries or areas with 90,000 persons or more in 2013 are considered.

Population Trends

- Current population is at 7.4 billion, gaining 81 million people per year
- Population growth is inevitable until 2050
- Half of the population growth to 2100 will be in 8 countries: Nigeria, India, the United Republic of Tanzania, the Democratic Republic of Congo, Niger, Uganda, Ethiopia and the United States of America
- For the medium scenario, the population is expected to reach 9.6 billion by 2050 with 23 million being added per year
- Longevity is increasing while fertility is declining, reducing the growth rate but increasing the median age



Population or Consumption?

IPAT equation – Measure of impact humans have on the environment

Impact = Population x Affluence x Technology

**As populations become more affluent and consume more technology,
environmental impact increases**

Population AND Consumption.

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World Consumption

- Since 1970 world consumption has increased 21.3 fold, to US\$37.5 trillion
- Population, however, has only increased 1.85 fold since 1970
- Most of that increase consumption lies with the high income population
- The middle income has increased almost 10 fold while the low income has barely increased consumption
- The population of the middle income has increased the greatest, from 2.55 billion to 4.9 billion



Consumption - the Down Side

- Developing countries are still far behind the industrialised world
- Many undeveloped countries, particularly in Africa, have slowed or stagnated
- The average African household consumes 20% less than 25 years ago
- Over 20% of the global population have been left out of this move to a better life



Consumption - the Down Side

- Over a billion people are deprived of basic needs
- 3/5 of the 4.4 billion people in developing countries lack basic sanitation
- 1/3 lack access to drinking water
- 1/4 have inadequate housing
- 1/5 have no access to medical services
- 1/5 do not attend school to grade 5



Poverty in Developed Countries

- 7-17% in developed nations are poor
- Sweden (7%) is 13th in average income
- The US has the highest average income and the highest poverty (17%)
- The UK has 14.3% poverty and the Netherlands 7% poverty with the same income levels
- Australia had 13.9% poverty in 2014



Pollution and the Poor

- Generally the poor are most exposed to pollution
- 80% of the 2.7 million annual victims of air pollution are rural poor in developing countries
- Lead poisoning is affecting child development in developing countries; in Bangkok up to 70,000 children lose 4 or more IQ points due to atmospheric lead
- In Latin America up to 15 million children under 2 are at similar risks
- In China, chemical plants are causing soil, air and water pollution in rural areas, increasing rates of cancer and respiratory disease



Environmental impact and the Poor

- Poverty also means increased degradation of the environment as the poor cannot afford to find alternatives to desertification or deforestation, control erosion or replenish depleted soils
- Many of the poor are forced to live on agriculturally marginal lands resulting in greater desertification and poverty



Ecological Footprint

Ecological Footprint - the impact of a person or community, of a set standard of living, on the environment, expressed as the amount of land/water required to sustain their use of natural resources

(lower the better!)

- World global bio-capacity – 1.7gha/person!
- USA – 8.00gha/person
- Puerto Rico – 0.04gha/person
- Australia - 6.84gha/person

One global hectare (gha) represents the average productivity of all biologically productive areas (measured in hectares) on earth in a given year.

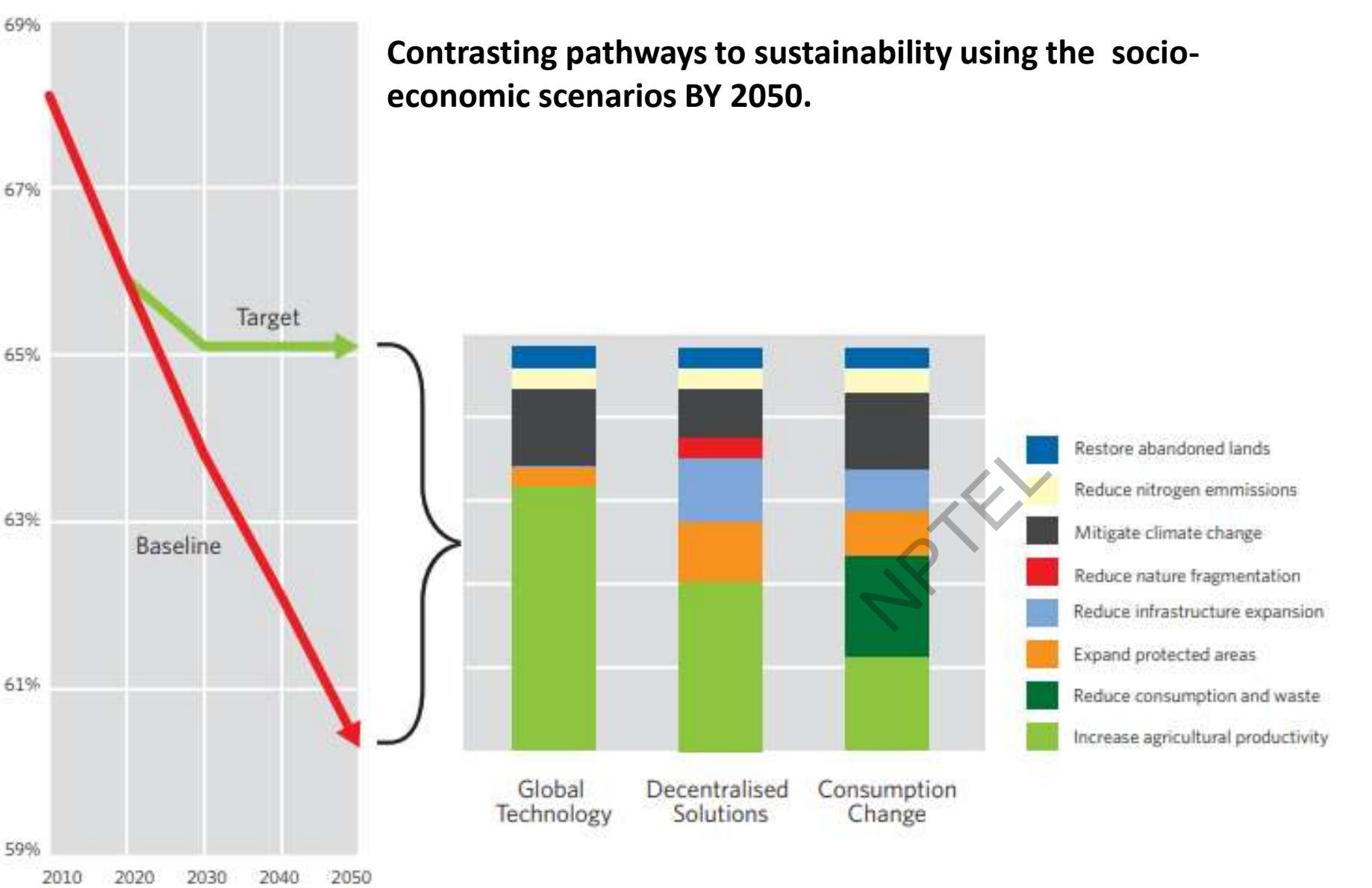
- [http://www.wwf.org.au/our work/people and the environment
/human footprint/footprint calculator/](http://www.wwf.org.au/our_work/people_and_the_environment/human_footprint/footprint_calculator/)



For the Future

- Consumption is currently increasing faster than population
- As developing country populations become more affluent, they will consume more
- The increasing gap between rich and poor is increasing social conflict
- Can we provide for the needs of 9.5 billion people, let alone the demands?
- Significant behavioural and economic changes will be needed





Global Biodiversity Outlook 4



DRIVERS

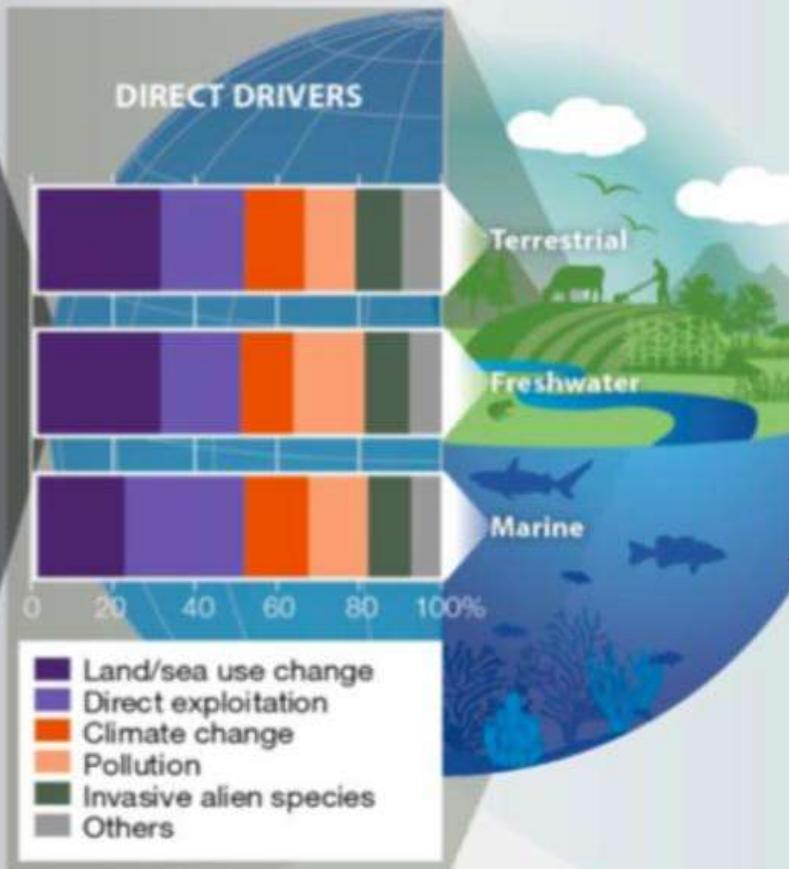
INDIRECT DRIVERS

Demographic and sociocultural

Economic and technological

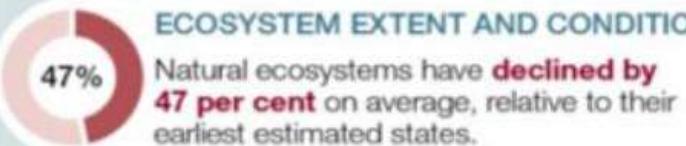
Institutions and governance

Conflicts and epidemics



EXAMPLES OF DECLINES IN NATURE

ECOSYSTEM EXTENT AND CONDITION



SPECIES EXTINCTION RISK

Approximately 25 per cent of species are already threatened with extinction in most animal and plant groups studied.

ECOLOGICAL COMMUNITIES

Biotic integrity—the abundance of naturally present species—has declined by 23 per cent on average in terrestrial communities.*

BIO MASS AND SPECIES ABUNDANCE

The global biomass of wild mammals has fallen by 82 per cent.* Indicators of vertebrate abundance have declined rapidly since 1970



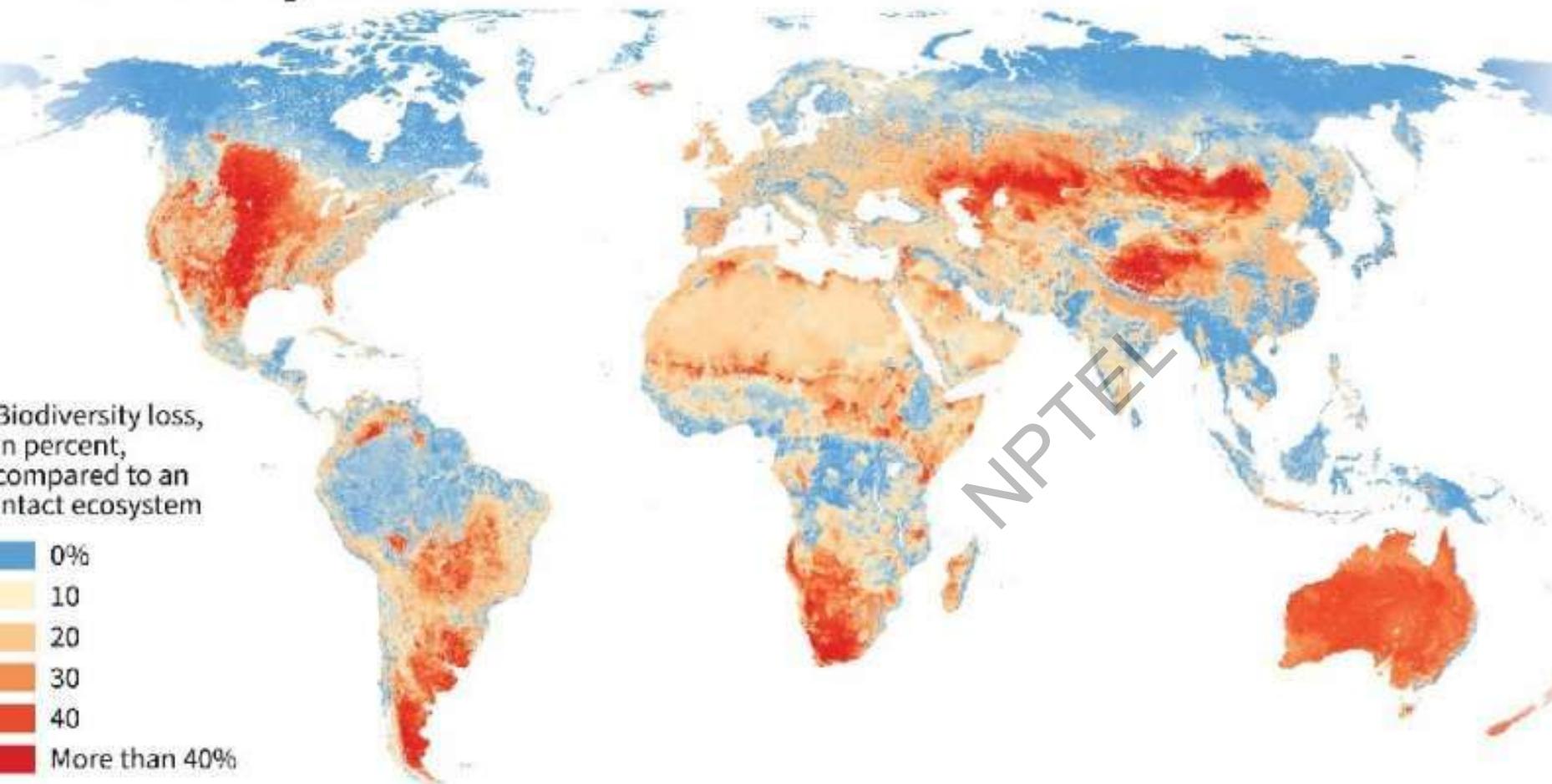
NATURE FOR INDIGENOUS PEOPLES AND LOCAL COMMUNITIES

72 per cent of indicators developed by indigenous peoples and local communities show ongoing deterioration of elements of nature important to them

* Since prehistory
UN Biodiversity Report- IPBES report



Biodiversity loss



Biodiversity loss,
in percent,
compared to an
intact ecosystem

0%
10
20
30
40
More than 40%

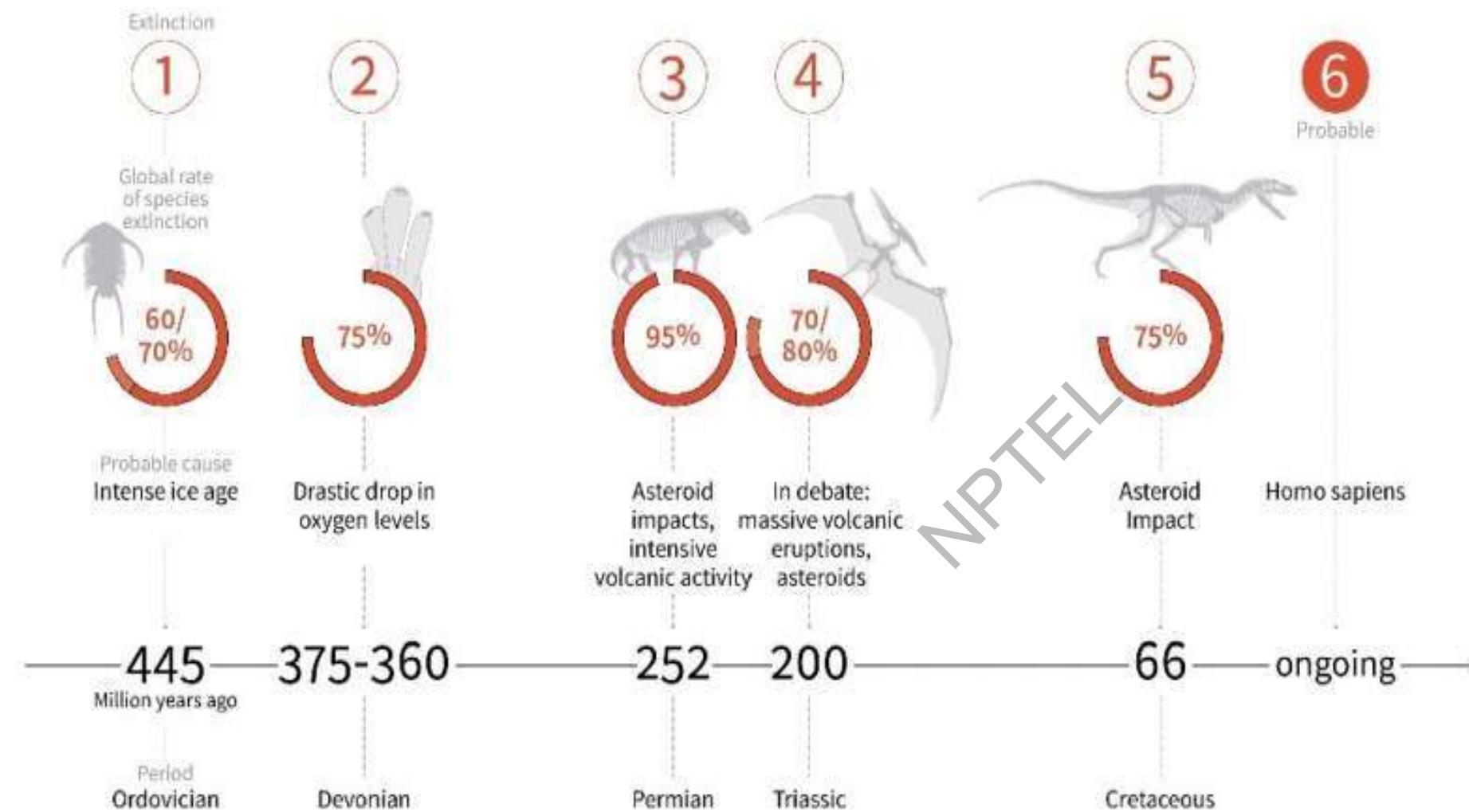
Source: National History Museum Data Portal. Data from 2016

© AFP



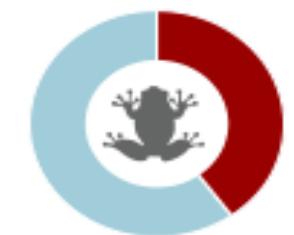
Earth's "mass extinctions"

During the last 500 million years, Earth has experienced five periods when at least half the living creatures were wiped out



One in four species are at risk of extinction

Species assessed by the IUCN Red List



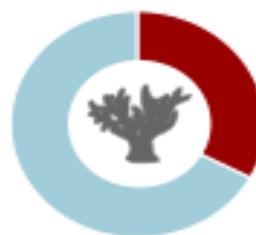
Amphibians

40%



Conifers

34%



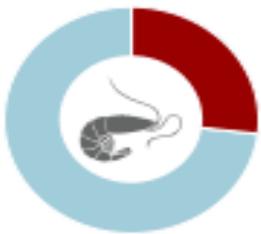
Reef corals

33%



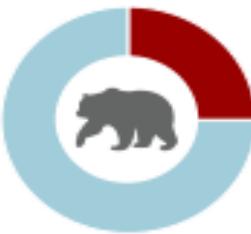
Sharks and rays

31%



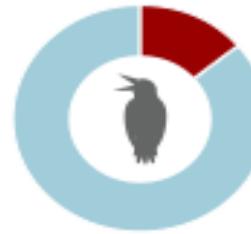
Selected crustaceans*

27%



Mammals

25%



Birds

14%

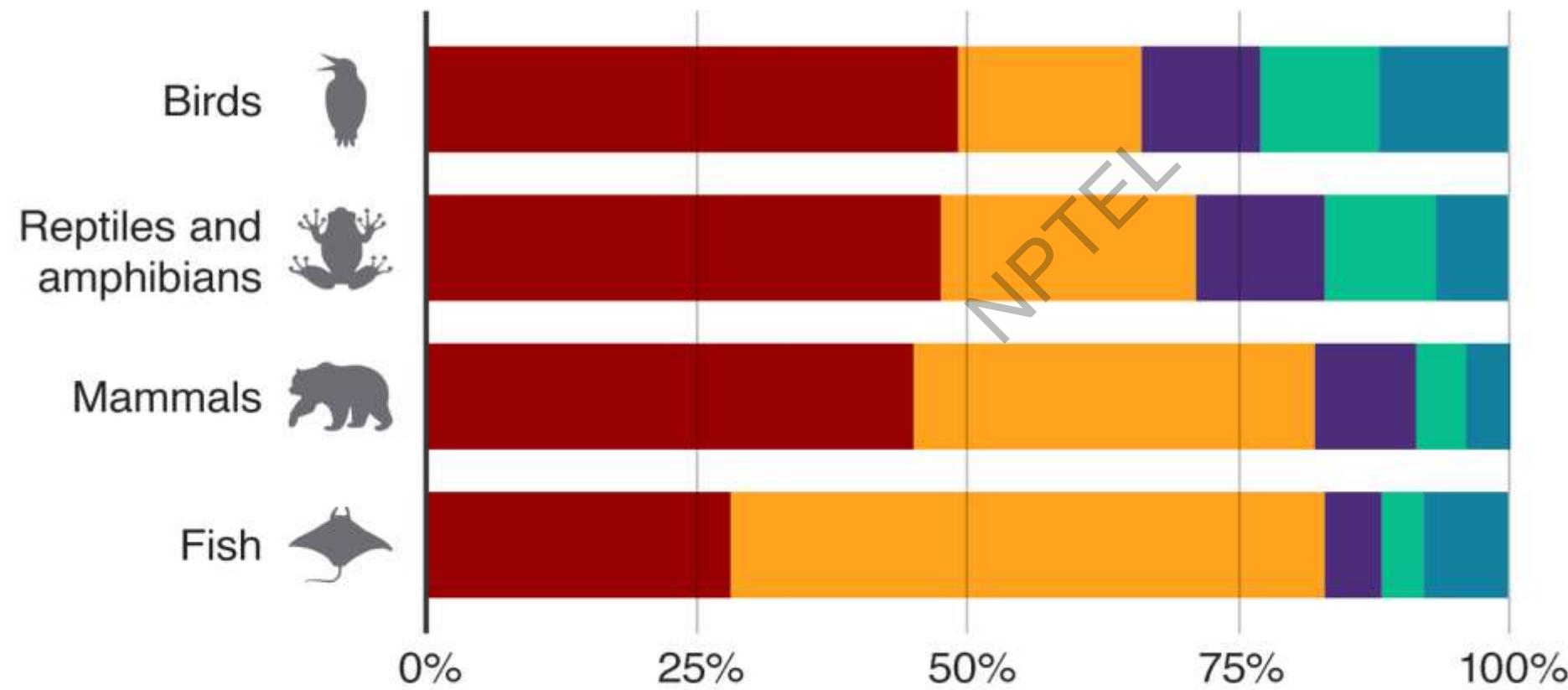
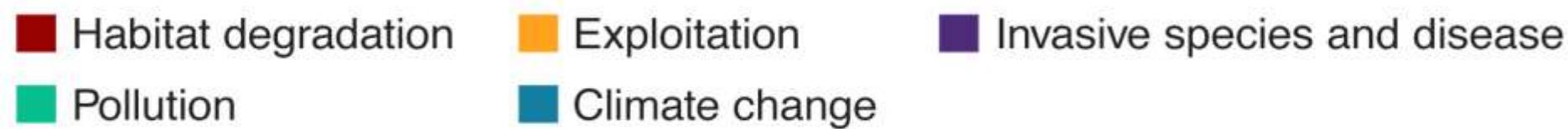
*Assessed species include lobsters, freshwater crabs, freshwater crayfishes and freshwater shrimps

Source: IUCN Red List of Threatened Species

BBC

Habitat loss is a major threat to biodiversity

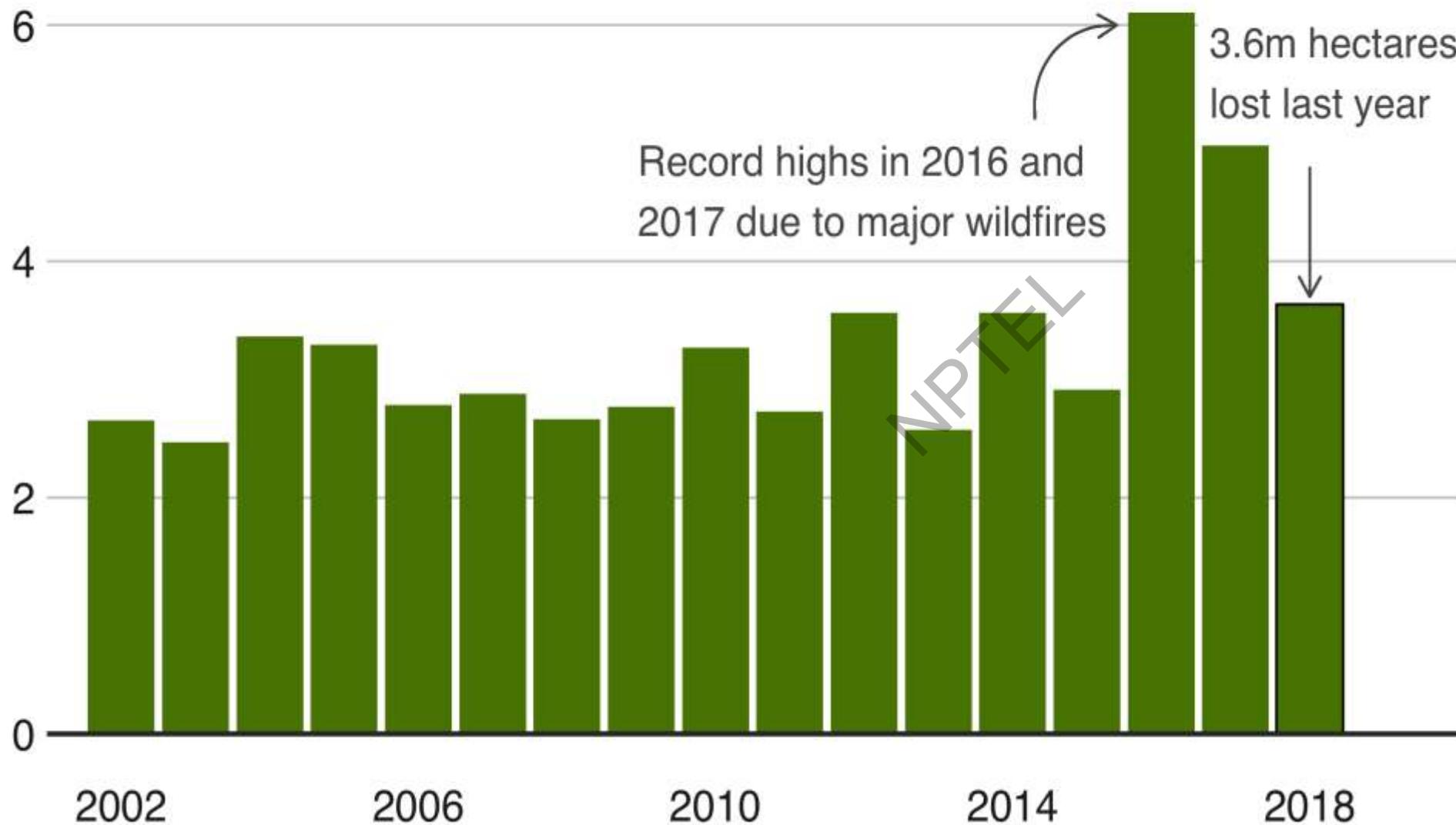
The Living Planet Report assesses key drivers of species decline



Note: A sample of 3,789 populations evaluated by the Living Planet Index

Belgium-sized area of forest destroyed in 2018

Tropical primary forest loss, millions of hectares



Source: Global Forest Watch, University of Maryland

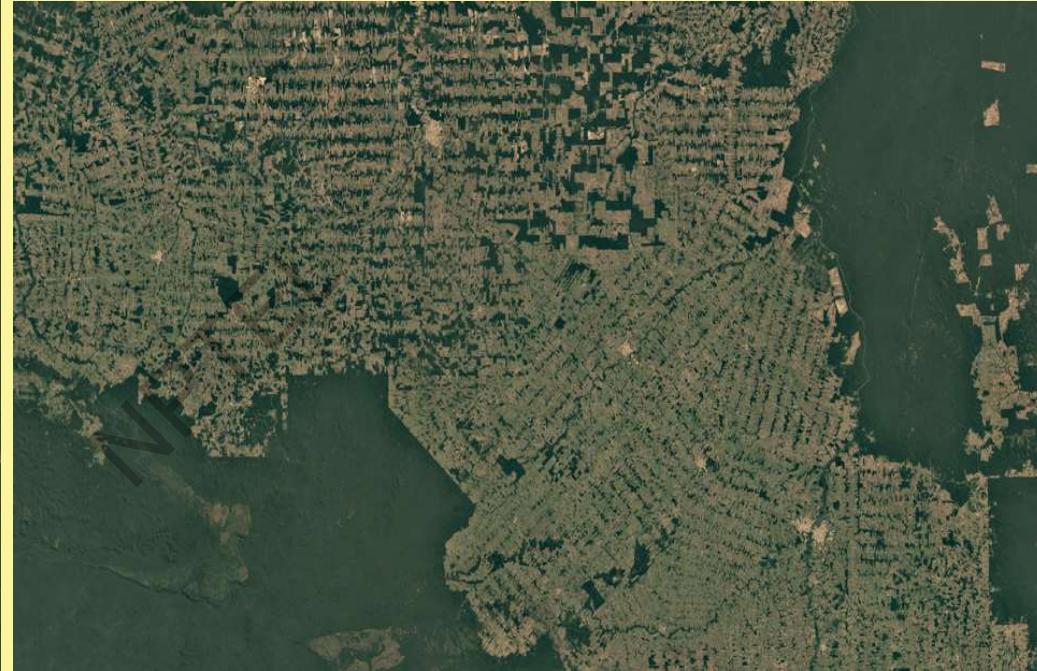
BBC

Some of the last great rainforests are being wiped out

1984

Amazon region

2018



Trees are being lost as forests are cut down for growing crops or for pastures to graze cattle, as well as for logging and mining.





Brazil's thriving soy industry threatens its forests and global climate targets

April 18, 2016 12:43pm AEST

<https://theconversation.com/brazils-thriving-soy-industry-threatens-its-forests-and-global-climate-targets-56973>



Conclusions

- Overall growth rate appears to be slowing but not as rapidly as originally estimated
- Currently population is not going to stabilise but continue to grow
- Significant effort by governments will be required to ensure growth slows to or below replacement level
- Even at replacement level, population will stabilise between 8 and 11 billion people
- As populations increase, it will be increasingly difficult to meet basic needs for water, shelter, food, clothing, energy and space





NPTEL ONLINE CERTIFICATION COURSES

Introduction to Environmental Engineering and Science – Fundamentals and Sustainability Concepts

Dr. Brajesh Kumar Dubey
Department of Civil engineering
IIT Kharagpur

Week-3 Topics

Ecology, Population & Environmental Chemistry
Lecture 15 : Environmental Chemistry

Approaches in Environmental Chemistry

- Chemistry is the study of the composition, reaction, and characteristics of matter. It is important because the ultimate fate of many chemicals discharged to air, water, and treatment facilities is controlled by their reactivity and chemical speciation.
- Two different approaches are used in evaluating a chemical's fate and treatment: **Kinetic and Equilibrium**.
- Kinetic deals with rate of reactions
- Equilibrium deals with the final results

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Activity and Concentration

Activity – “effective concentration”

Concentration can be related to activity using the activity coefficient γ , where $[a] = \gamma (c)$

Activity - a

Concentration - c

Activity is designated by {} brackets, and concentration by [] brackets.

Activity coefficient, γ , depends on the solution's ionic strength.

The ionic strength of a solution (referred as μ) has a unit of moles/Liter and is a measure of the long range electrostatics interactions in that solutions.

Ionic strength, $\mu = 1/2 \sum_i C_i Z_i^2$

$\frac{1}{2} \sum_i C_i Z_i^2$



- C is the molar concentration of an ionic species “i” in the solution.
- Z_i is the charge of the ion.
- Fresh water typically have ionic strength of 0.001- 0.01M and the ocean has an ionic strength of approximately 0.7M.
- The method for calculating the activity coefficient for electrolyte and non electrolyte is presented in next slide.

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STEP 1

After deciding whether ionic strength effects are important in a particular situation, calculate ionic strength from a

$$\mu = \frac{1}{2} \sum_i C_i Z_i^2$$

Estimate ionic strength after measuring the solution's total dissolved solids or conductivity

STEP 2

If species is an electrolyte, γ will always be ≤ 1

If species is a nonelectrolyte, γ will always be ≤ 1

| For low ionic strengths, $\mu < 0.1 \text{ M}$, | For high ionic strengths, $\mu < 0.5 \text{ M}$, | For all ionic strengths, use |
|---|---|----------------------------------|
| Use the Güntelberg (or similar) approximation: | Use the Davies (or similar) approximation: | $\log \gamma_i = k_s \times \mu$ |
| $\log \gamma_i = \frac{-Az_i^2 \sqrt{\mu}}{1 + \sqrt{\mu}}$ | $\log \gamma_i = -Az_i^2 \left(\frac{\sqrt{\mu}}{1 + \sqrt{\mu}} - 0.3\mu \right)$ | |



Example 3.1 - Calculate the ionic and all the individual activity coefficients for a 1 L solution of water at 15 °C in which 0.01 mole of FeCl_3 and 0.005 mole of H_2SO_4 are dissolved.

After the two compounds are placed in water, they will completely dissociate to form 0.01 M Fe^{3+} , 0.01 M H^+ , 0.03 M Cl^- , and 0.005 M SO_4^{2-} . The ionic strength is calculated by

$$\mu = 1/2 [0.01(3 +)^2 + 0.01(1 +)^2 + 0.03(1 -)^2 + 0.005(2 -)^2] = 0.075 \text{ M}$$

This ionic strength is relatively high but still much less than that of seawater. The Güntelberg approximation is useful for calculating activity coefficients for electrolytes when $\mu < 0.1 \text{ M}$.
The value of "A" depends on temperature and equals 0.49 at 0°C, 0.50 at 15°C, and 0.51 at 25°C:

$$\gamma(\text{H}^+) = 0.78, \gamma(\text{Cl}^-) = 0.78, \gamma(\text{SO}_4^{2-}) = 0.38, \gamma(\text{Fe}^{3+}) = 0.11$$



The activity coefficients of ions with higher valence deviate much more from 1.0 for a given ionic strength; that is, for electrolytes, use of activity coefficients is much more important for ions with a higher valance, because they are strongly influenced by the presence of other ions. Thus, while at a particular ionic strength, it may not be important to calculate activity coefficients for monovalent ions, it may be very important for di-, tri-, and tetravalent ions.

NPTEL



Example 3.2 – An air stripper is used to remove benzene (C_6H_6) from seawater and freshwater. Assume the ionic strength of seawater is 0.7 M and that of freshwater is 0.001 M. What is the activity coefficient for benzene in seawater and freshwater?

Solution –

Because benzene is a nonelectrolyte, use the expression given before to determine the activity coefficients. The value for k_s (the salting-out coefficient) for benzene is 0.195.

$$\log \gamma = k_s \times \mu$$

$$\log \gamma = 0.195 \times (0.001 \text{ M}); \text{ results in } \gamma (\text{freshwater}) = 1$$

$$\log \gamma = 0.195 \times (0.7 \text{ M}); \text{ results in } \gamma (\text{seawater}) = 1.4$$

$$\mu < 0.1 \text{ M}$$



Therefore, determining activity coefficients for non electrolytes becomes important for solutions with high ionic strengths. For most dilute environmental systems, activity coefficients for electrolytes and non electrolytes usually are assumed to be equal to 1. Places where they can gain importance are in the ocean, estuaries, briny groundwater, and some recycled or reused waste streams.

For freshwater, the activity coefficient does not deviate much from 1. It turns out there is little deviation for *nonelectrolytes* when

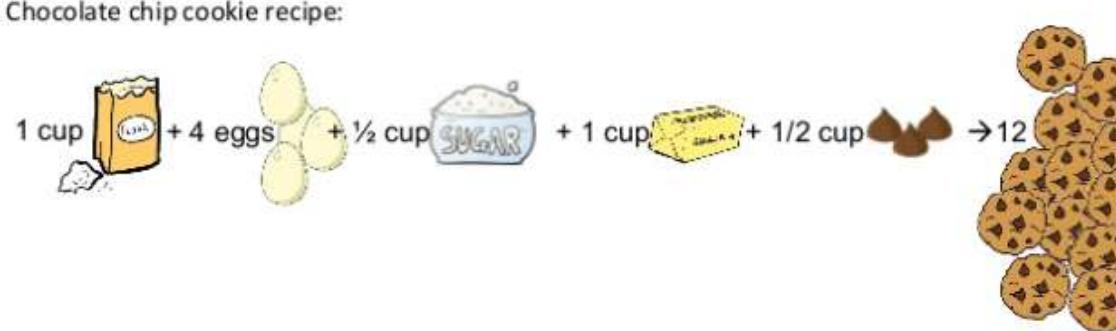


Stoichiometry

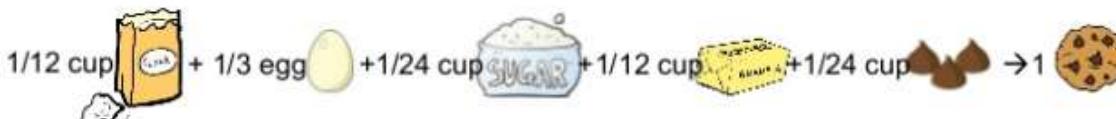
Stoichiometry is founded on the **law of conservation of mass** where the total mass of the reactants equals the total mass of the products, leading to the insight that the relations among quantities of reactants and products typically form a ratio of positive integers. This means that if the amounts of the separate reactants are known, then the amount of the product can be calculated. Conversely, if one reactant has a known quantity and the quantity of the products can be empirically determined, then the amount of the other reactants can also be calculated.

STOICHIOMETRY

Chocolate chip cookie recipe:

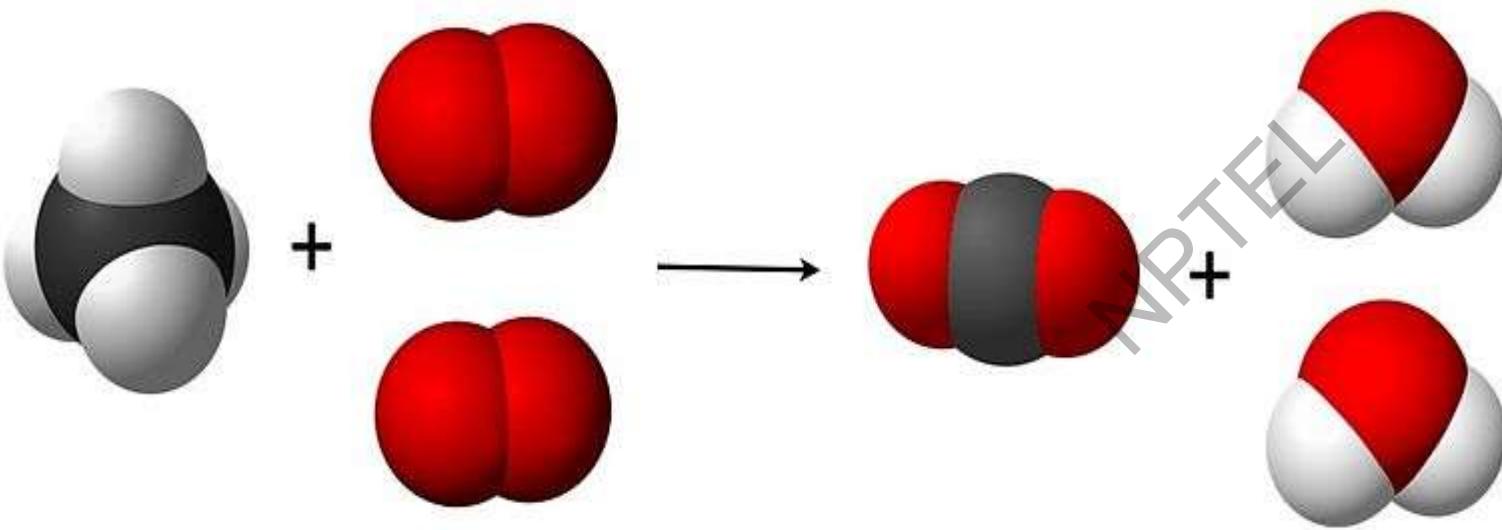


If I want only 1 cookie, then how much of each ingredient is needed?



Combustion reaction of methane

One molecule of methane reacts with two molecules of oxygen gas to yield one molecule of carbon dioxide and two molecules of water.



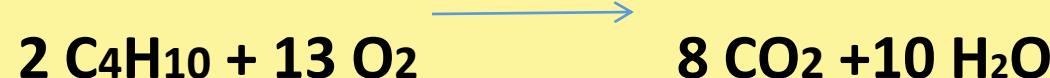
Numerical: What mass of carbon dioxide would be produced if 100g of butane(C_6H_{10}) is completely oxidized to carbon dioxide and water?

Solution:

1. First write down the reaction:



Then balance it



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2. Find the grams per mole for the butane:

$$\text{C}_4\text{H}_{10} = 4 \cdot 12 + 10 \cdot 1 = 59 \text{ g/mol}$$

We already know that there are 44 grams per mole of CO₂, so we don't need to calculate that again. Two moles of butane (2 mol * 58 g/mol = 116g) yields 8 moles of carbon dioxide (8mol * 44 g/mol= 352 g CO₂). So, we can set up the following proportion:

$$116 \text{ g C}_4\text{H}_{10} / 352 \text{ g CO}_2 = 100 \text{ g C}_4\text{H}_{10} / \text{X(?) g CO}_2$$

$$\text{X} = 100 \cdot 352 / 116 = 303 \text{ g of CO}_2 \text{ produced.}$$



Thermodynamic laws

Thermodynamics deals with conversion of energy from one form to another.

First law of thermodynamics

Energy is conserved; it may be converted from one form to another, but the total amount in a closed system is constant. In an open system, one must account for fluxes across the system boundaries

For an open system:

$$dU = dQ - dW + dG$$

Where, U= internal energy content, Q= heat content, W= work done, and G= energy of chemical inputs



- **What does it mean?**

This relationship demonstrates that the chemical potential (the energy within the chemical bonds of a molecule) constitutes a part of the total energy of the system.

In a closed system (in which case, the third term on the right would be absent), reactions that change the chemical potential without changing the internal energy content must result in equivalent changes in heat content and in the pressure-volume work performed.

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Second law of thermodynamics

All systems tend to lose useful energy and approach a state of minimum free energy or an equilibrium state.

Thus, a process will proceed spontaneously (without energy put into the system from the outside) only if the process leads to a decrease in the free energy of the system (that is, **del G<0**).

Formal definition of Gibbs free energy:

$$G = \sum_i \mu_i * N_i = H - T * S$$

H= Enthalpy

S=Entropy

T=Temperature



What does it mean?

The energy of inter and intra molecular bonds that binds various atoms and molecules together is termed **enthalpy**. While **entropy** represents disorder of the system.

Enthalpy in chemical systems

The first law of thermodynamics lets us say that the energy in the reactant on the left side of the equation, plus any heat added to the system, should equal the energy contained in the reaction products on the right side, plus any work done during the reaction.



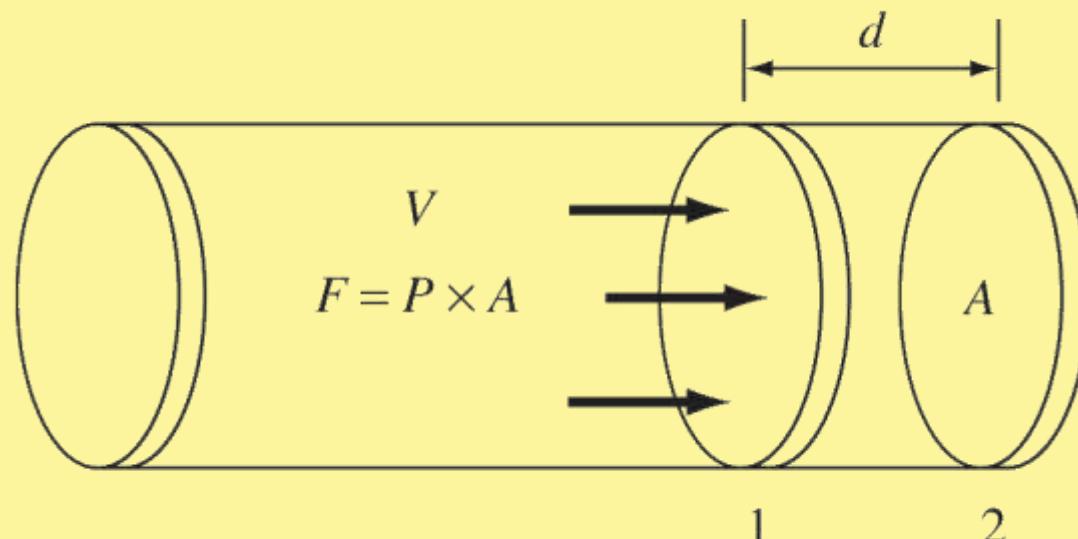


Figure: 02-01

Copyright © 2008 Pearson Prentice Hall, Inc.

$$U_1 + Q = U_2 + W$$

U_1 = Internal energy of the chemical system at the beginning.

U_2 = Internal energy at the end

Q = Heat absorbed during the reaction

W = Work done by the system during reaction

To analyze the work done by expansion , consider the cylinder in figure containing a volume of gas V exerting a pressure P against a piston with area A . The force exerted by gas on the piston is $P * A$. If the piston moves a distance d , then, since work is force* distance, we can write
 $W= Fd = PAd = P(V_2 - V_1)$



Now first equation becomes

$$(U_2+PV_2) - (U_1+PV_1) = Q$$

If we define the enthalpy ,H , of a system as

$$H = U + PV$$

Then,

$$H_2 - H_1 = \Delta H = Q$$

That is, the change in enthalpy during a constant pressure reaction is equal to the heat absorbed by the system.

When **ΔH is positive**, heat is absorbed and the reaction is said to be endothermic.

When **ΔH is negative**, heat is liberated and the reaction is said to be exothermic.

Change in the enthalpy, $H_2 - H_1$ is called the heat of reaction.



Standard Enthalpies for Selected Species (kJ/mol)

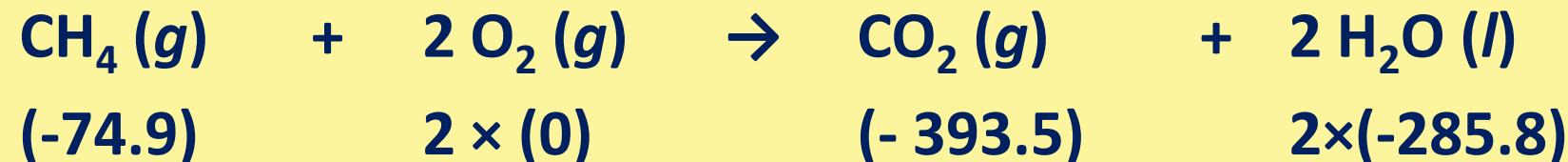
| Substance | State ^a | H_{298}^0 | Substance | State ^a | H_{298}^0 |
|-----------------------------|--------------------|-------------|----------------------|--------------------|-------------|
| Ca^{2+} | <i>aq</i> | -543.0 | HCO_3^- | <i>aq</i> | -691.1 |
| CaCO_3 | <i>s</i> | -1207 | H_2O | <i>l</i> | -285.8 |
| Ca(OH)_2 | <i>s</i> | -986.6 | H_2O | <i>g</i> | -241.8 |
| C | <i>s</i> | 0 | NO | <i>g</i> | 90.4 |
| CO | <i>g</i> | -110.5 | NO_2 | <i>g</i> | 33.9 |
| CO_2 | <i>g</i> | -393.5 | NO_2^- | <i>aq</i> | -106.3 |
| CO_2 | <i>aq</i> | -412.9 | N | <i>g</i> | 472.6 |
| CH_4 | <i>g</i> | -74.9 | N_2 | <i>g</i> | 0 |
| C_2H_4 | <i>g</i> | 52.3 | N_2O | <i>g</i> | 81.55 |
| CH_3COOH | <i>aq</i> | -488.5 | NH_3 | <i>aq</i> | -80.8 |
| $n\text{-C}_4\text{H}_{10}$ | <i>g</i> | -124.7 | O | <i>g</i> | 247.5 |
| $i\text{-C}_4\text{H}_{10}$ | <i>g</i> | -131.6 | O_2 | <i>g</i> | 0 |
| H | <i>g</i> | 217.9 | O_3 | <i>g</i> | 142.9 |
| H^+ | <i>aq</i> | 0 | OH^- | <i>aq</i> | -229.9 |
| H_2 | <i>g</i> | 0 | SO_2 | <i>g</i> | -296.9 |

^ag = gas, *aq* = aqueous, *s* = solid, *l* = liquid.



Example: Find the heat of the reaction when methane is oxidized to CO₂ and liquid.

The reaction is written here and the standard enthalpies taken from previous table



Notice we have used the enthalpy of liquid water for this calculation. The heat of reaction is the difference between the total enthalpy of the reaction products and reactants:

$$[(-393.5) + 2 \times (-285.8)] - [(-74.9) + 2 \times (0)] = -890.2 \text{ kJ/mol of CH}_4$$

Since the heat of reaction is negative, heat is released during combustion (*i.e.*, it is exothermic).



Find the heat of combustion when methane is burned. (To be solved by readers)

Just repeat the method of previous slide but this time the water will remain in the gaseous state.

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Application of the concept of Enthalpy

When a molecule is dissociated by absorbing a photon of energy, the process is called a photochemical reaction or photolysis

For a photon to be able to cause photolysis, it must have at least as much energy as the change in enthalpy for the reaction.

We know

$$E = hc/\lambda,$$

Where, E= Energy of a photon (J)

h = Planck's Constant (6.6×10^{-34} J-s)

C= Speed of light (3×10^8 m/s)

λ = Wavelength (m)

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For photolysis to take place , maximum wavelength is given by

$$\lambda \leq hc/E$$

We can equate the energy in the photon with the enthalpy change.

$$\lambda \leq hc/E$$

$$1.19 * 10^{-4} (\text{kJ.m/mol}) / (\Delta E^0 (\text{kJ/mol}))$$

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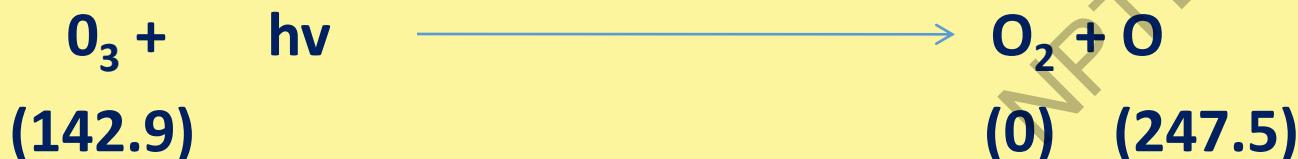


How does incoming solar radiation gets absorbed by stratospheric ozone ?

Photolysis of Ozone

What maximum wavelength of light would be capable of causing photolysis of ozone O_3 into O_2 and O ?

Write the reaction, including enthalpies from the table give in the previous slides.



The enthalpy change is $\Delta H^\circ = 247.5 - 142.9 = 104.6 \text{ kJ/mol}$

Since , ΔH° is positive , its endothermic reaction (absorbs energy).

$$\lambda \leq 1.19 * 10^{-4} \text{ kJ.m/mol} / 104.6 \text{ kJ/mol} = 1.13 * 10^{-6} \text{ m} = 1.13 \text{ um}$$



Chemical Equilibrium

Chemical equilibrium is a state in which the rate of the forward reaction equals the rate of the backward reaction. In other words, there is no net change in concentrations of reactants and products.



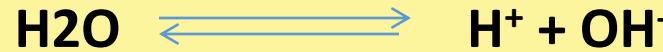
$$K = [C]^c[D]^d/[A]^a[B]^b \text{ ...at equilibrium}$$

Where, [] represent concentration of the substance at the equilibrium expressed in moles per liter(Morality). K is called as equilibrium constant.



Acid Base Reactions

Water dissociates slightly into hydrogen ions (H^+) and hydroxide ions(OH^-).



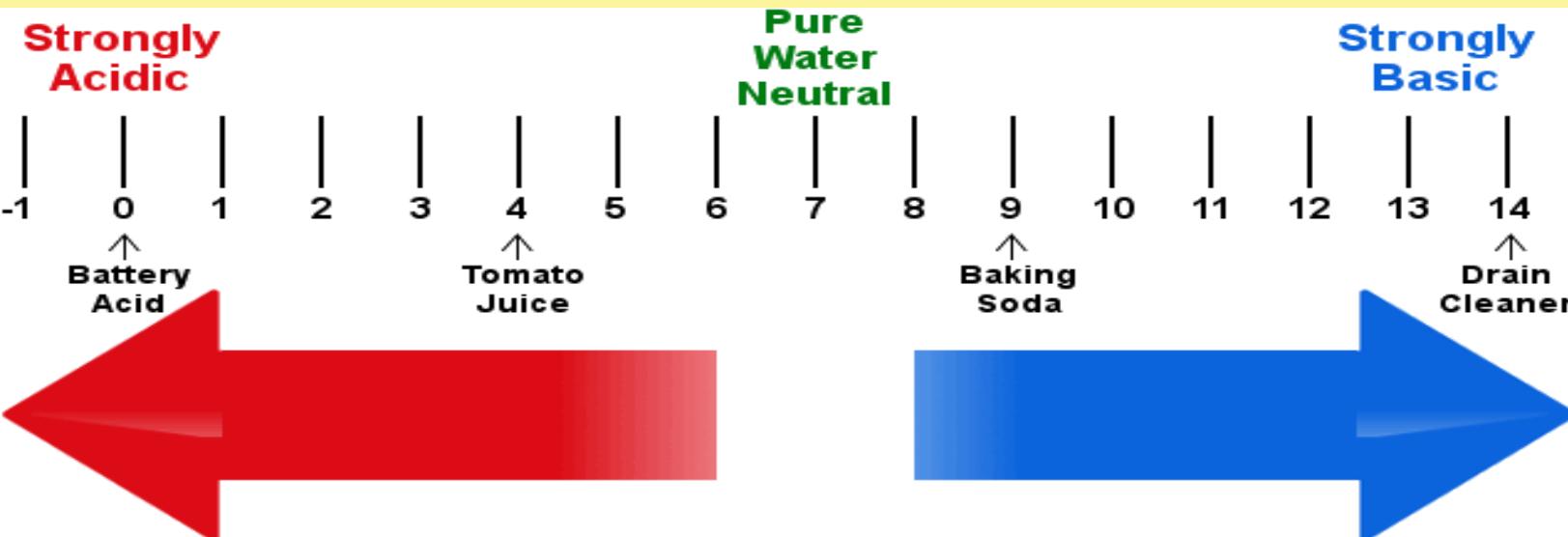
The corresponding equilibrium expression for the reaction is

$$[H^+][OH^-]/[H_2O] = K$$

$$pH = -\log [H^+]$$

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

With pH scale, it is easy to specify whether a solution is acidic, basic , or neutral.



In a neutral solution, the concentration of hydrogen ions $[H^+]$ equals the concentration of hydroxide ions $[OH^-]$.

$$[H^+] [OH^-] = [H^+] [H^+] = [H^+]^2 = 10^{-14}$$

$$[H^+] = 10^{-7}$$

Question:

Find the hydrogen ion concentration and the hydroxide ions concentration in tomato juice having pH of 4.1 (Exercise for the reader).

Solution :

$$7.94 \times 10^{-5} \text{ mol/L}$$

$$1.26 \times 10^{-10} \text{ mol/L}$$



Dissociation Constants and Chemical Formulas for Some Acids of Environmental Importance

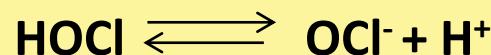
| Acid | Formula | pK_{a1} | pK_{a2} | pK_{a3} |
|-------------------|--|-----------|-----------|-----------|
| Nitric acid | HNO_3 | -1.30 | — | — |
| Hydrochloric acid | HCl | <0 | — | — |
| Sulfuric acid | H_2SO_4 | <0 | 1.99 | — |
| Phosphoric acid | H_3PO_4 | 2.16 | 7.20 | 12.35 |
| Arsenic acid | H_3AsO_4 | 2.24 | 6.76 | — |
| Citric acid | $\text{C}_3\text{H}_4\text{OH}(\text{COOH})_3$ | 3.13 | 4.72 | 6.33 |
| Acetic acid | CH_3COOH | 4.76 | — | — |
| Carbonic acid | H_2CO_3 | 6.35 | 10.33 | — |
| Hydrogen sulfide | H_2S | 6.99 | 12.92 | — |
| Hypochlorous acid | HOCl | 7.60 | — | — |
| Ammonium ion | NH_4^+ | 9.26 | — | — |
| Silicic acid | H_4SiO_4 | 9.84 | 13.20 | — |

Acid-base reactions are among the most important in environmental engineering.
 Most aquatic forms of life are very sensitive to the change in pH of their habitat .
 To protect local ecosystems, waste neutralization before release is common.



Example:

Chlorine is the active ingredient in most household bleach and is one of the most commonly used and inexpensive chemical disinfectant for water. The chlorine is in the hypochlorous acid form, HOCl, and hypochlorous acid is a much better disinfectant than hypochlorite, OCl⁻ its conjugate base. If bleach is used to disinfect water, below, what pH should the water be maintained so that at least 95% of the chlorine added is in the hypochlorous acid form?



The equilibrium constant equation is

$$K = [\text{OCl}^-] [\text{H}^+]/[\text{HOCl}] = 10^{-7.60} \text{ (From previous table)},$$

Which rearranges to

$$[\text{H}^+] = [\text{HOCl}] K / [\text{OCl}^-]$$

We can then solve for [H⁺] when [HOCl]/[OCl⁻] = 95/5 = 19, so

$$[\text{H}^+] = 19 * 10^{-7.60} = 4.77 * 10^{-7} = 10^{-6.32}$$

If the pH is kept below 6.3, then more than 95% percent of the chlorine will be in the HOCl form.



Kinetics

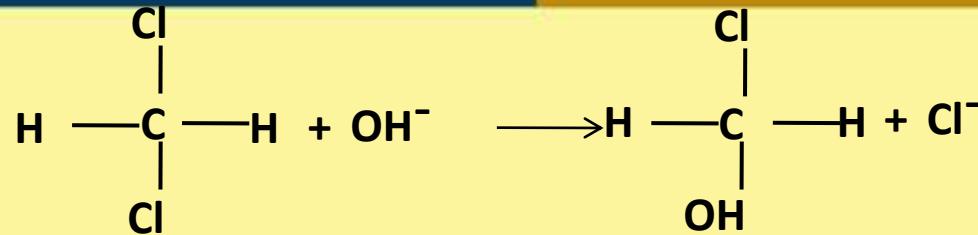
The kinetic approach to environmental chemistry addresses the rate of reactions.

Concepts include the rate law, zero-order and first order reactions, half-life, and factors that affect the rate of reaction.

THE RATE LAW

The rate law expresses the dependence of the reaction rate on measurable, environment parameters. Of particular interest is the dependence of the rate on the concentrations of the reactants. Other parameters that may influence the reaction rate include temperature and the presence of catalysts (including microorganisms).





$$\begin{aligned}
 R &= k[\text{DCM}][\text{OH}^-] = -d[\text{DCM}]/dt \\
 &= -d[\text{OH}^-]/dt = d[\text{CM}]/dt = d[\text{Cl}^-]/dt
 \end{aligned}$$

Where R is the rate of reaction, k is the rate constant for this particular reaction, $[\text{DCM}]$ is the concentration of DCM, $[\text{OH}^-]$ is the concentration of hydroxide ion, $[\text{CM}]$ is the concentration of CM, $[\text{Cl}^-]$ is the concentration of chloride ion, and t is time. The negative signs in Equation 3.35 indicate that the products' concentrations are decreasing over time.

The bold portion on the left side of Equation 3.35 is referred to as the reaction's *rate law*, which expresses the dependence of the reaction rate on the concentrations of the reactants.



To generalize these terms, a hypothetical rate law can be constructed for a generic irreversible reaction of a moles of species A reacting with b moles of species B to yield products, P . The rate law is written as

$$R = k[A]^a[B]^b$$

This reaction would be termed a th order with respect to A and b th order with respect to B . The over all order of the reaction would be $(a+b)$. This reaction is termed an elementary reaction because the reaction order is controlled by the stoichiometry of the reaction. That is a , equals the molar stoichiometric coefficient of species A and b equals the molar stoichiometric coefficient for B .



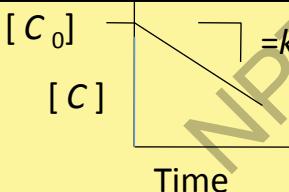
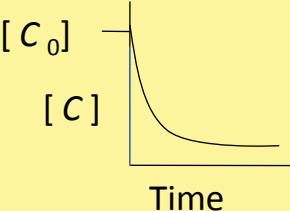
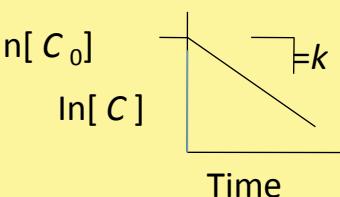
ZERO-ORDER AND FIRST-ORDER REACTIONS

$C \rightarrow \text{products}$

$$\frac{d[C]}{dt} = -k[C]^n \quad \dots \dots \dots (1)$$

ZERO-ORDER REACTION

$$\frac{d[C]}{dt} = -k \quad \dots \dots \dots (2)$$

| Reaction Order | Rate Law | Integrated form of Rate Law | Plot of Concentration versus Time | Linearized Plot of Concentration versus Time | Half-Life, t | Example Units of Rate Constant, k |
|----------------|---------------------------|-----------------------------|--|--|----------------------|---|
| Zero | $\frac{d[C]}{dt} = -k$ | $[C] = [C_0] - kt$ |  Same as $[C]$ vs. time | | $\frac{0.5[C_0]}{k}$ | moles/L-s mg/L-s |
| First | $\frac{d[C]}{dt} = -k[C]$ | $[C] = [C_0]e^{-kt}$ |  |  | $\frac{0.693}{k}$ | $s^{-1}, \text{min}^{-1}, \text{h}^{-1}, \text{day}^{-1}$ |



FIRST- ORDER REACTION

If $n = 1$, Equation (1) becomes

$$d[C]/dt = -k[C]$$

This is the rate law for a first-order reaction. Here, the rate of disappearance of C with time is first-order with respect to $[C]$, and the overall order of the reaction is first-order.

Equation (1) can be rearranged and integrated for the same two conditions used in Equation (2) to obtain an expression that describe the concentration of C with time:

$$[C] = [C]_0 e^{-kt}$$

Here, k is the first-order reaction rate constant and has units of time^{-1} (for example, h^{-1} , day^{-1}).



Example :

How long will it take the carbon monoxide (CO) concentration in a room to decrease by 99 percent after the source of carbon monoxide is removed and the windows are opened?

Assume the first-order rate constant for CO removal (due to dilution by incoming clean air) is 1.2/h. No chemical reaction is occurring.

Solution:

This is a first-order reaction,

Let $[CO]_0$ equal the initial CO concentration.

When 99 percent of the CO goes away,

$[CO] = 0.01 \times [CO]_0$. Therefore,

$$0.01 = [CO]_0 = [CO]_0 e^{-kt}$$

Where $k = 1.2/h$. Solve for t , which equals 3.8 h.



HALF-LIFE AND ITS RELATIONSHIP TO THE RATE CONSTANT

It often is useful to express a reaction in terms of the time required to react one-half of the concentration initially present.

The half-life, $t_{1/2}$, is defined as the time required for the concentration of a chemical to decrease by one-half (for example, $[C]=0.5 \times [C]_0$).

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The relationship between half-life and the reaction rate constant depends on the order of the reaction.

For zero-order reactions , the half-life can be related to the zero-order rate constant, k . To do this, substitute $[C]=0.5 \times [C_0]$ into Equation 3.42:

$$0.5[C_0] = [C_0] - kt_{1/2}$$

Equation 3.50 can be solved fro the half-life:

$$t_{1/2} = \frac{0.5 \times [C_0]}{k}$$

Likewise, for a first-order reaction, the half-life can be related to the first-order rate constant, k . In this case, substitute $[C] = 0.5 \times [C_0]$ into Equation 3.44:

$$0.5[C_0] = [C_0]e^{-kt}$$

The half-life for a first-order relationship then is given by

$$t_{1/2} = \frac{0.693}{k}(3)$$



Example:

Subsurface half-lives for benzene, TCE, and toluene are listed as 69, 231, and 12 days, respectively. What are the first-order rate constants for all three chemicals?

Solution:

The model only accepts concentration-dependent, first-order rate constants. Thus, to solve the problem, convert half-life to a first-order rate constant with Eq. (3)

For benzene,

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{69 \text{ days}} = 0.01/\text{day}$$

Similarly, $k_{\text{TCE}} = 0.058/\text{day}$ and $k_{\text{toluene}} = 0.058/\text{day}$.



Example :

The 2011 Fukushima nuclear disaster was the largest since the Chernobyl disaster of 1986. It occurred after the Tohoku earthquake and tsunami and consisted of several nuclear meltdowns and releases of radioactive materials. One and a half years after the disaster, Japan still bans the sale of 36 fish species caught off the coast of Fukushima, destroying the social and economic livelihood of the local region. A 2012 scientific paper reported two Greenland fish close to shore had gathered than 25,000 becquerels (Bq) per kg of fish (wet weight) from the presence of radioactive cesium. This is 250 times greater than the government's safety limit (in comparison, the U.S. threshold is 1,200 Bq per kg of fish (wet weight)). Assume that the only reaction by which cesium is lost from the fish is through radioactive decay and the half-life for this isotope is 3 years. **Calculate the concentrations of radioactive cesium in a Fukushima fish after 5 years.**

(Note: A becquerel is a measure of radioactivity; 1 becquerel equals 1 radioactive disintegration per second.)

Would regulators allow this fish to be consumed in Japan or the United States?



Solution:

Because the half-life equals 3 years, the rate constant k can be determined from Equation 3.53:

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{3 \text{ year}} = 0.23/\text{year}$$

Therefore:

$$\begin{aligned}[{}^{137}\text{Cs}]_{t=5} &= [{}^{137}\text{Cs}]_{t=0} \exp(-kt) \\&= 25,000 \text{ Bq/L} \\&\times \exp\left(\frac{-0.23}{\text{year}} \times 5 \text{ year}\right) \\&= 7,916 \text{ Bq/L}\end{aligned}$$



This fish is not safe to eat according to regulations in Japan and the United States. The value greatly exceeds the threshold values of 100 and 1,200 Bq per Kg of fish (wet weight) set by each country's government. A problem to work on at home is, how many years would it take this fish to reach safe levels set by each country?

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