Thermodynamics and work energy (exergy) of Ecosystems Presentations at SYKE's Sustainability Workshop 24.-26. September

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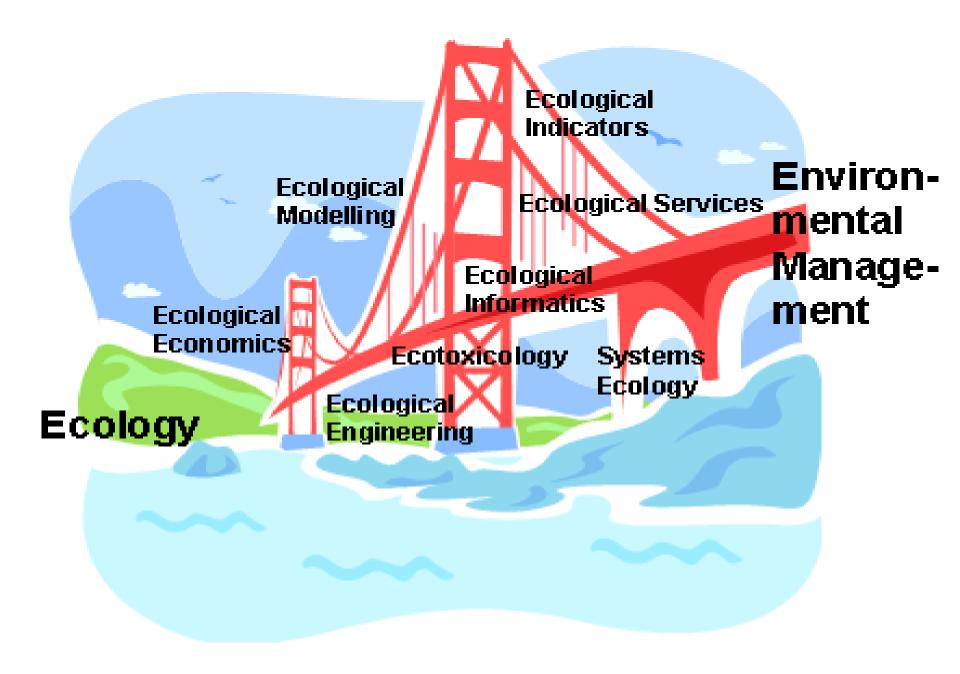
# Systems Ecology builds on four columns:

# • 1) Thermodynamics • 2) Biochemistry • 3) Hierarchy Theory • 4) Network Theory

# Application of Systems Ecology is very important in:

- **1. Ecosystem Management**
- 2. Ecological Modelling
- 3. Ecological Economics
- 4. Ecological Engineering
- 5. Selection of ecological indicators
- 6. Ecological Informatics
- 7. Ecosystem Services

These ecological sub-disciplines form a very important bridge between environmental management and ecology



#### 1. Law of Thermodynamics: Conservation of Energy and Matter

#### Conservation of energy:

#### $\Delta \mathbf{U} = \Delta \mathbf{Q} + \Delta \mathbf{W}$

• where U is the energy and  $\Delta U$  is the increase of energy,  $\Delta Q$  is the amount of heat received from the environment and  $\Delta W$  is the amount of work received from the environment.

#### • $dU = dQ - dW (ML^2/T^2)$

where

- dQ = thermal energy added to the system
- dU = increase in internal energy of the system
- dW = work done by the system on its environment.

#### **Conservation of matter**

- Accumulation = input output
- dC /dt = ( input output)/ V
- V \* dc / dt = input output + formation transformation (M/T)

#### Different forms of (work) energy and their intensive and extensive variables

- Energy form Extensive variable Intensive variable
- Heat
- Expansion
- Chemical

- Entropy (J / K) Volume (m3)
- Moles (M)

- Electrical
- Potential
- Kinetic /s2)

Charge ( Ampere sec) Mass (kg)(Gravity) Mass (kg)

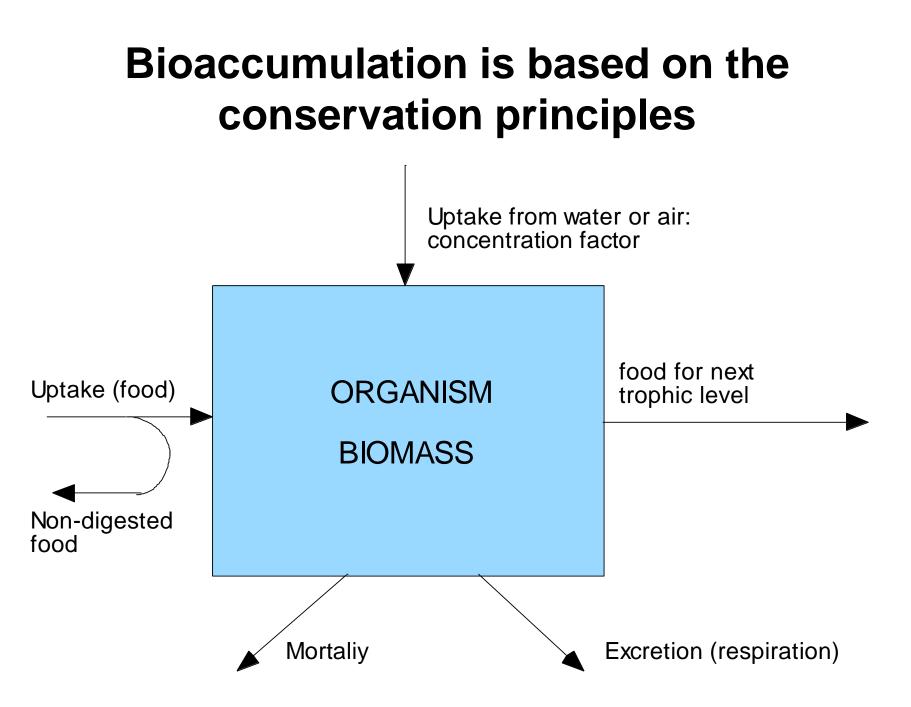
Temperature (K) Pressure (Pa= kg /( s2 m)) Chemical potential (J / moles) Voltage (Volt) (Height) (m2 / s2) 0.5(Velocity)^ (m2

Potential and kinetic energy are denoted mechanical energy

#### Energy conservation: fate of solar energy

SUNLIGHT 1.97 Reflection and evaporation 1.95

Gross production (0.024) = Net production (0.020) + Respiration (0.004)



#### Early and mature ecosystem

Early ecosystems: low biomass, high production relative to biomass, simple network, low biodiversity, few feed backs, r-strategists, low information content

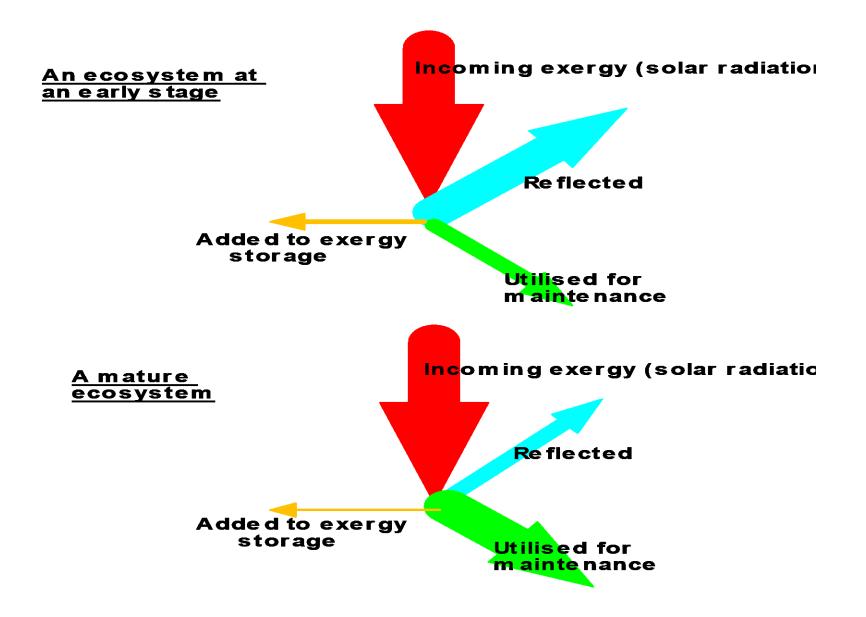
Mature ecosystems: high biomass, low production relative to biomass, complex network, high biodiversity, many feed backs, K-strategists, high information content

## Odum's attributes correspond to three growth /development forms:

1) Growth of biomass, notice that more

biomass means that the ecosystem is able to capture more free energy (work capacity, also called exergy from the sunligth, but also more free energy is needed for maintenance.

- 2) Growth of the network
- 3) Growth of the content of information
- Notice that 2) and 3) increase the use of the free energy of the sunlight captured
- Energy balance for early and mature stage see next figure



#### 4. Irreversibility and Order. The Second Law of Thermodynamics

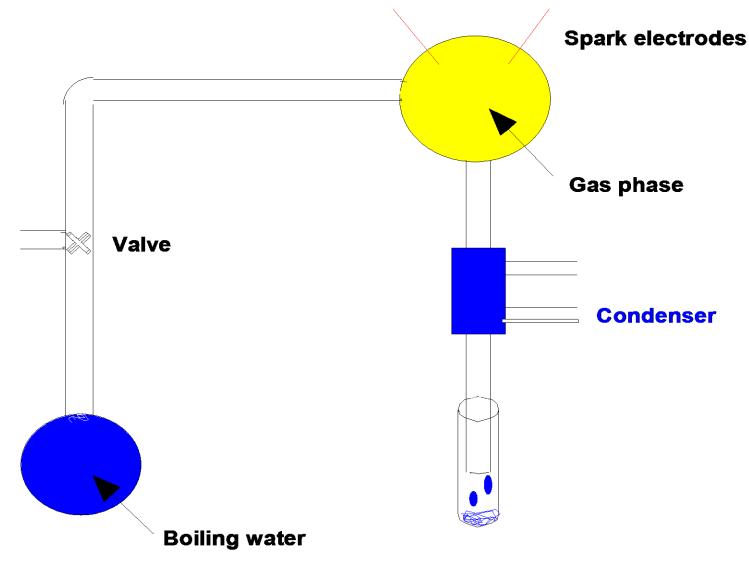
The Second Law of Thermodynamics states that all system will by all its processes lose order and gain disorder or expressed differently: all system will lose energy that can do work (exergy) to energy that cannot do work. The system will move towards the thermodynamic equilibrium corresponding to dG = 0 and a minimum value of free energy (work energy).

ALL PROCESSES ARE IRREVERSIBLE

#### The second law applied on ecosystems:

»It looks like ecosystems violate the first law of »thermodynamics because they are moving » away from thermodynamic equilibrium by »formation of a biological structure, implying »that they gain chemical (work) energy. »Ecosystems receive, however, work energy as solar »radiation,which delivers the energy for formation » of the biological structure and also the work »energy needed for maintenance of the system far 

#### An example: the Stanley Miller and Harold Urey Experiment



#### The third Law of Thermodynamics

 The third law of thermodynamics states that the entropies, S0, of pure chemical compounds are zero, and that entropy production,  $\Delta$ S0, by chemical reactions between pure crystalline compounds are zero at absolute temperature, 0 K. Remember in this context, that temperature is a measure of how fast atoms are moving, where 0K corresponds to no movement at al. The third law implies, since both So = 0 (absolute order) and  $\triangle$ S0 = 0 (no disorder) generation), that disorder does not exist and cannot be created at absolute zero temperature.

An inflow of work energy implies that the work energy is used to:

- 1) to maintain the system (ecosystem or any system) far from thermodynamic equilibrium – it covers the respiration
- The work energy in our food covers our need for maintenance work energy
- 2) if more work energy is available we can see for instance a spring day the the extra work energy is used to build new structure.

How can we describe thermodynamically the building of new structure?

 The new structure contains work energy in form of mainly chemical (work) energy of the many complex biochemical compounds. The work energy can be calculated as a gradient (for chemical energy is chemical potential) times an amount (moles for chemical energy). It is denoted exergy, because it uses other reference state than classical thermodynamics, where the concept of free energy is applied.

#### Information contains work energy

- Ecosystems (living organisms) possess an enormous amount of information. Information is work energy according to Boltzmann. It is covered by Kullbach's measure of information or by Boltzmann's equation: kT In N
- Where N is the number of microstates that we do know.

## Work energy including the work energy of information is denoted eco-exergy

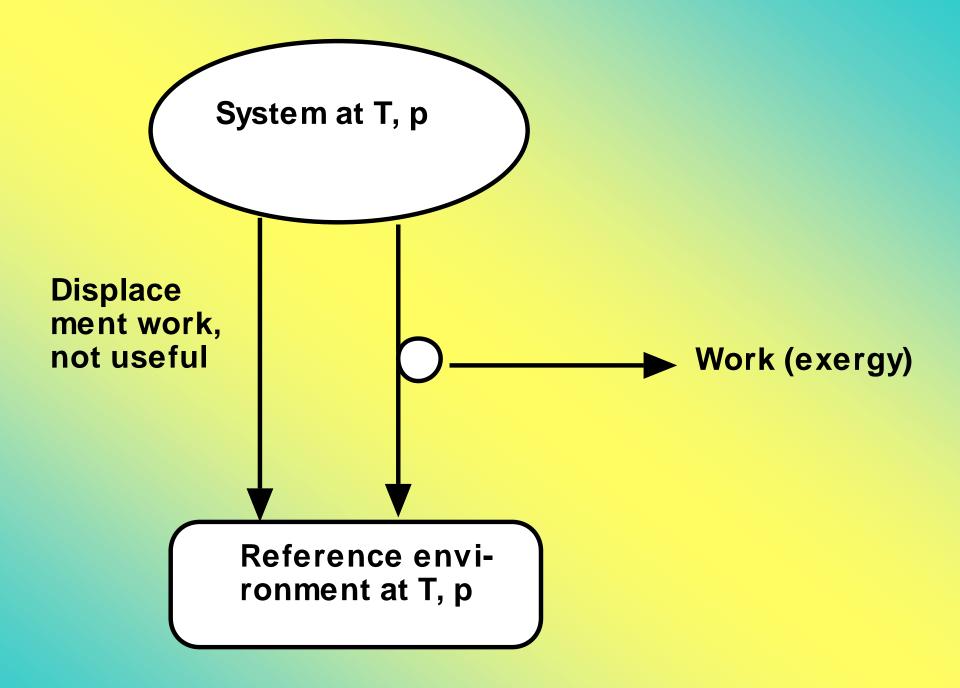
 Living organisms can utilize this information to control and perform life processes. Therefore, we should of course used eco-exergy for ecosystems. Information is used to make it possible for system to operate - think about a computer and a watch. They are useless without the information and contains more work energy than just the work energy of the material.

#### What is exergy?

- Exergy is work capacity energy that can do work. It can therefore be found as the gradient (= difference in potential)x extensive descriptor, dependent on the energy form, for instance
- Chemical energy=  $(\mu_1 \mu_2) N or$
- **Pressure energy**=  $(p_1-p_2)(-V)$
- Potential energy=  $(h_1 h_2) m g$
- Electrical energy=  $(V_1 V_2) Q$

#### We may distinguish between technological exergy and ecoexergy:

- Technological exergy uses the environment as reference state and is useful to find the first class energy (work) that a power plant can produce
- Eco-exergy uses as reference state the same ecosystem with the same temperature and pressure but at thermodynamic chemical equilibrium. Notice that ecoexergy includes the work energy of information.



#### How to find the exergy?

- i=n i=n
- $\mathbf{E}\mathbf{x} = \sum (\boldsymbol{\mu}_1 \boldsymbol{\mu}_2) \ \mathbf{C}_i = \mathbf{R}\mathbf{T} \sum \mathbf{C}_i \ln \mathbf{C}_i / \mathbf{C}_{i,o}$
- i=0 i=0

• 
$$\mathbf{A} = \sum \mathbf{c}_i \quad \mathbf{p}_i = \mathbf{c}_i / \mathbf{A}$$

- Ex = A RT  $\sum pi \ln pi / pio + A \ln A / Ao = ARTK,$ i=1
- where K is Kullbach's measure of information
- So, eco-exergy is biomass times the information (RTK)
- RTK is abbreviated β. β can be found for different organisms.

#### **Calculations of eco-exergy**

- R is 8.34 J / mole K or 8.34 kJ 10^(-8)/ g presuming a molecular weight of 10^5. It implies that the ß-values or the specific eco-exergy in detritus equivalents for an organism
- =RTK = 8.34 \*300\*10^(-8) ln20 \*AMS / 18.7 = 4.00\*10^(-6)\*AMS
- where AMS is the number of amino acids in a coded sequence and  $\ln 20 = 3.00$ .  $\beta$  can also be found by Boltzmann's equation and approximately the same  $\beta$ -values are found

# ß-values found from the genome sizes I

<b>Organis</b>	ms Genom	<u>e Mb Re</u>	oeat %	ß

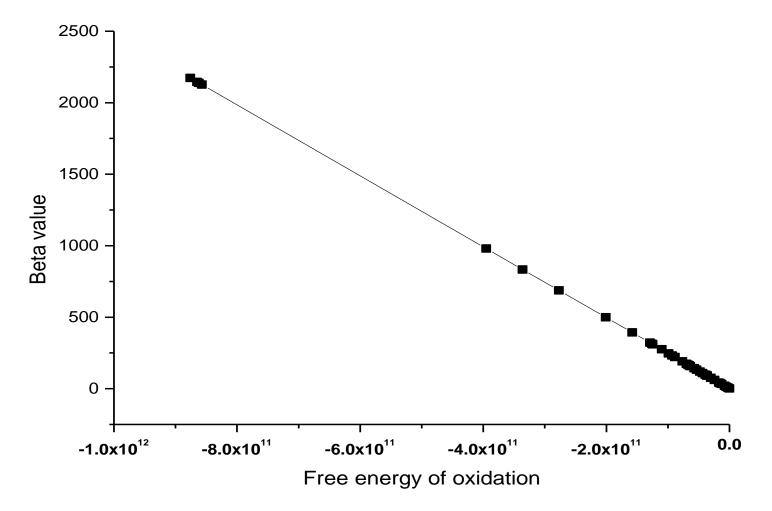
Human	2900	46	2173
Mouse	2500	38	2127
Tiger fish	400	9	<b>499</b>
Mosquito	280	16	322
Squirt	155	10	191
Fruit fly	137	2	184
Yeast	12	2	16
Amoeba	34	0.5	<b>46</b>

# ß-values found from the genome sizes I

Organisms Ge	enome	Mb Repeat <sup>o</sup>	<u>% ß</u>
Human	2900	<b>46</b>	2173
Mouse	2500	38	2127
Worm	97	0.5	153
Mustard weed	128	14	147
Rice	400	50	275
Virus			1.01
Reptiles			833*)
Birds			980*)
*) found indire	ctlv		

Eearly organims	Plants		Animals
Detritus		1.00	
Virus		1.01	
Minimal cell		5.8	
bacteria		8.5	
Archaea		13.8	
Protists Algae		20	
Yeast		17.8	
		33	Mesozoa, Placozoa
		39	Protozoa, amoebe
		43	Phasmida (stick insects)
Fungi, moulds		61	
		76	Nemertina
		91	Cnidaria (corals,sea anemones, jelly fish)
	Rhodophyta	92	
		97	Gastroticha
Prolifera, sponges		98	
		109	Brachiopoda
		120	Platyhelminthes (flatworms)
		133	Nematoda (round worms)
		133	Annelida (leeches)
		143	Gnathostomulida
	Mustard weed	143	
		165	Kinorhyncha
	Seedless vascula		-
	plants (incl.ferns)	158	
	,	163	Rotifera (wheel animals)
		164	Entoprocta
	Moss	174	•
		167	Insecta (beetles, flies, bees, wasps, bugs, ants)
		191	Coleodiea (Sea squirt)
		221	Lipidoptera (buffer fliés)
		232	Crustaceans
		246	Chordata
	Rice	275	
	Gynosperms (inl. pinus)	314	
	<b>3 1 ( 1 <i>)</i></b>	310	Mollusca, bivalvia, gastropodea
		322	Mosquito
	Flowering plants	393	•
	51	499	Fish
		688	Amphibia
		833	Reptilia
		980	Aves (Birds)
		2127	Mammalia
		2138	Monkeys
		2145	Anthropoid apes
		2173	Homo Sapiens
Theoie			-
Thesis		04-03-2	

The free energy of oxidation,  $\Delta G$ , of the amino acid chains making up the enzymes for various living organisms has been found. Reference system consists of air, water and sediment with the characteristic composition for the Earth 4 billion years ago



#### What is life?

1) The ability to metabolite, i.e. to draw nutrients from the environment, and convert them from chemical energy into other forms of energy, useful biochemical compounds and excrete waste products. The information embodied in the genes can be utilized to perform important life processes. 2) the ability to reproduce These two abilities are rooted in an enormous amount of (useful) information, that is able to control the processes needed to metabolite and reproduce.

#### What is life?

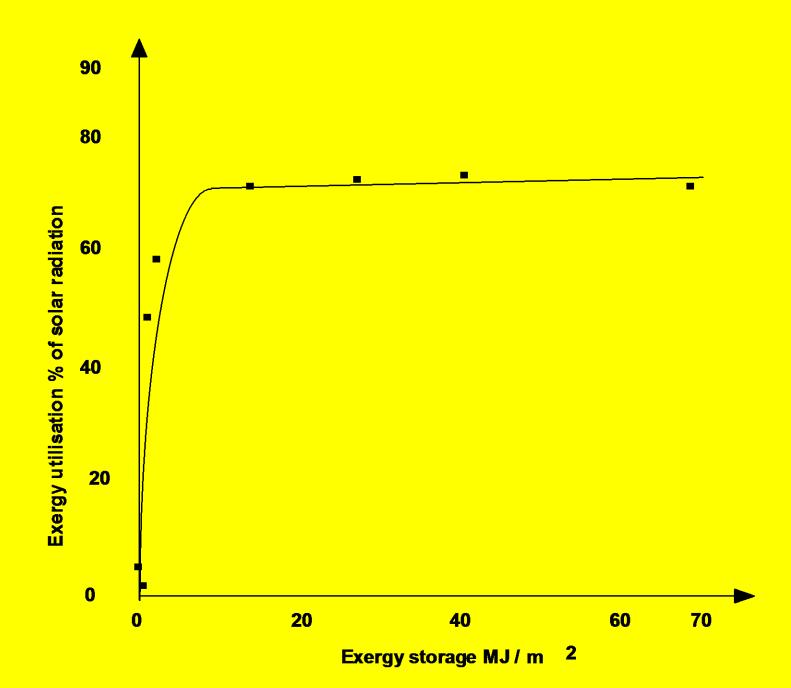
An iguane of 20 g will have an exerg content of 20.x18.7x833 kJ ≈ 312 GJ while a dead iguane will have only an exergy content of 374 kJ, although they have the same chemical composition, at least a few seconds after the iguane has died. The difference is rooted in the information or rather the difference in applicability of the information.

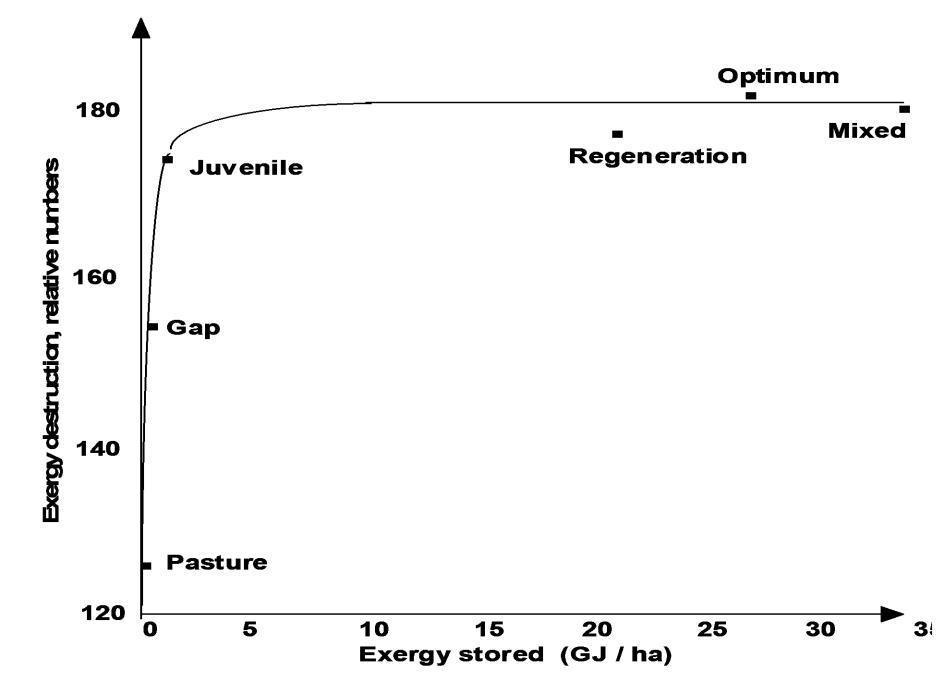
# The thermodynamic description of ecosystem development (growth):

 If an (eco)system received more work energy that it needs to cover the maintenance of the system far from thermodynamic equilibrium, then the surplus free energy or exergy is utilized to move the system further away from thermodynamic equilibrium, it means that the ecosystem gains eco-exergy or work energy capacity.

#### The ecosystem development described by a thermodynamic interpretation of the three growth forms.

- To illustrate the three growth forms thermodynamically, the following thermodynamic variables will be used:
- Eco-exergy (work capacity stored in the ecosystem relative to thermodynamic equilibrium)
- Power (through flow of useful energy = the sum of all free energy flows in the system)
- Emergy stored in the ecosystem
- Retention time
- Exergy consumption, loss or reduction due to maintenance of the system
- Entropy production
- Specific exergy of the ecosystem (eco-exergy stored divided by the biomass)
- Specific entropy production (entropy production / biomass).

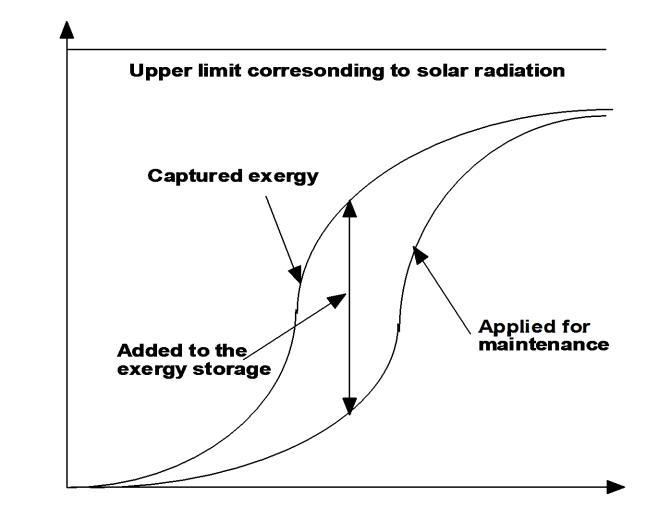




### Accordance between growth forms and thermodynamic variables

Growt	h Form I	Growth Form II	Growth Form III
Exergy storage Power / through	up	ир	up
flow	up	up	up
Emergy	up	equal, may	be up up
Exergy consumption	up	equal	equal
Retention time	equal	up	up
Entropy Production Exergy / Biomass=	up	equal	equal
specific exergy equal	-	ир	up
Entropy /biomass=			
spec. entropy prod.	equal	down	down

# Exergy utilization for an ecosystem under development



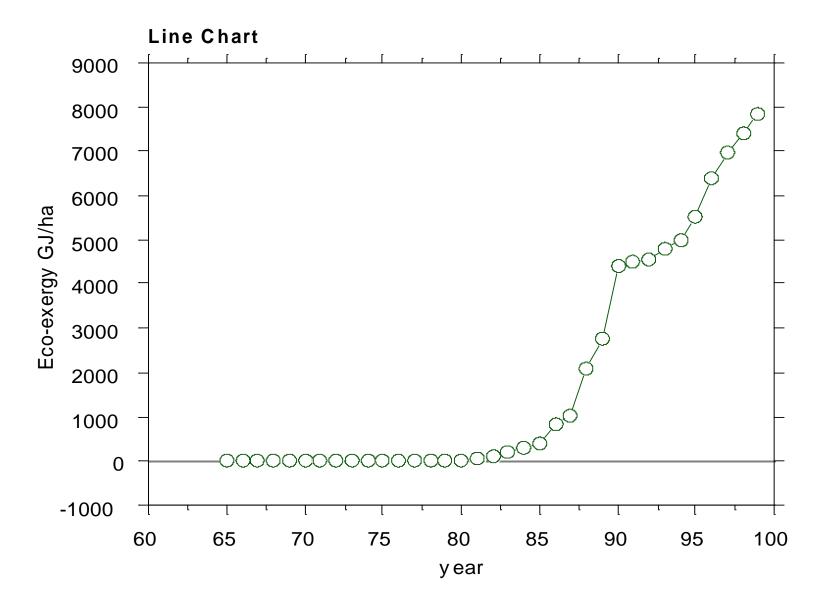


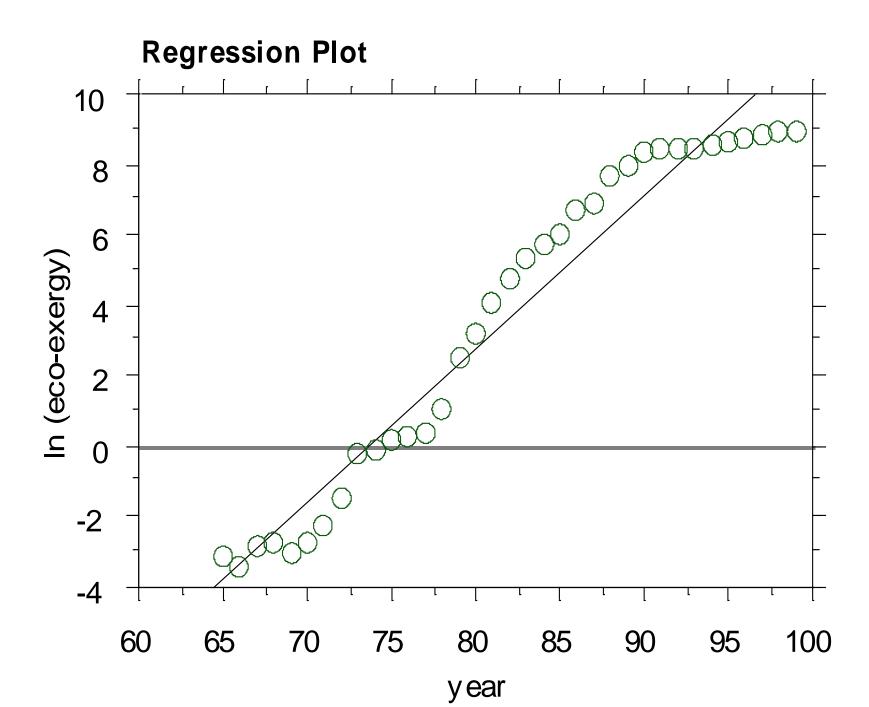
Time

#### Increase of eco-exergy in the spring



#### New ecosystems, Island Surtsey





### The Ecological Law of Thermodynamics

 ELT is a translation of Darwin's Theory to thermodynamics and at the same time an expansion from the organisms - or according to the neo-Darwinian interpretation the genes of the organisms - to the entire ecosystem, considering ?all the hierarchical levels

### **Darwin's Theory – Four principles I**

- 1) **The reproduction**; the organisms are able to reproduce and every population has such high fertility that its size would increase exponentially if not constrained.
- 2) The inheritance, the properties of the off springs are almost unchanged inherited from the parents or from the mother cell. The evolution would be impossible without the possibilities of building on the shoulders of what has already been achieved.

### **Darwin's Theory – four principles II**

- 3) **The variation**, not all organisms are identical but they are all more or less different. The variation is the prerequisite for selection. If all the organisms were identical, there would be no differences in survival and growth and therefore no selection, even among organisms of the same species. The selection takes place among the differences in properties of the phenotypes resulting in currently changing genomes generation after generation.
- **4) The competition**, i.e. the resources are limited. Therefore only some of the organisms can survive. The other will be out- competed or eliminated in the fight about the resources. The heritable variation affects the success of the organisms in surviving and multiplying.

### The Ecological Law of Thermodynamics (ELT)

 A system, that receives a through-flow of exergy (free energy, high quality energy) will try to utilize the exergy flow to move away from thermodynamic equilibrium, and if more combinations of components and processes are offered to utilize the exergy flow, the system will select the organization that gives the system as much exergy content (storage) as possible, i.e. maximizes dEx / dt.

### **Support to ELT I**

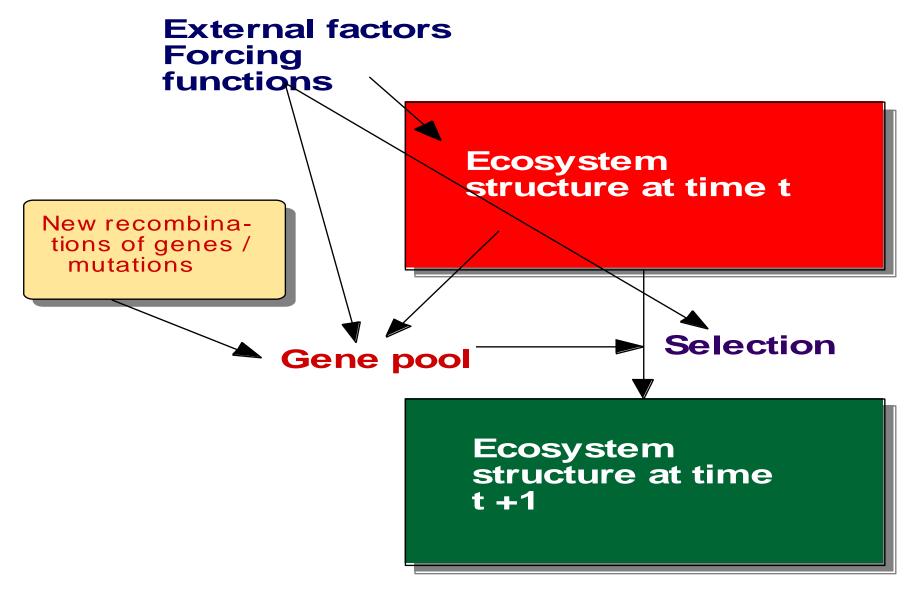
- 1. Size of genomes
- Biological evolution has been towards organisms with an increasing number of genes (Futuyima, 1986). If a direct correspondence between free energy and genome size is assumed

#### Support to ELT III: Yields of kJ and ATP's per mole of electrons by microbiological oxidation of, corresponding of CH2O

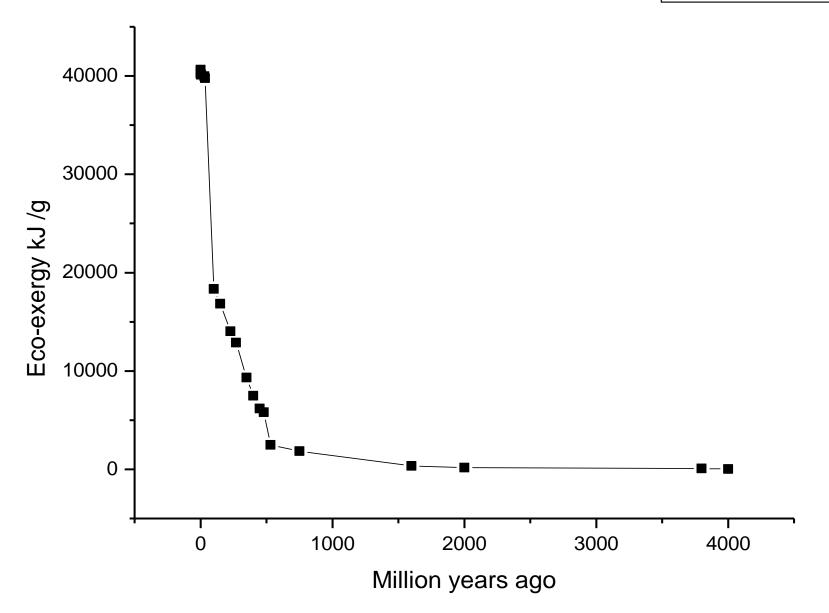
•	pH = 7.0 and 25 ° C.		
•	Reaction	kJ/mole e-	ATPs /mole e-
•	CH2O + O2 = CO2 + H2O	125	2.98
•	CH2O + 0.8  NO  3 - + 0.8  H + = CO2 + 0.4  N2 + 1.4  H2	119	2.83
•	CH2O + 2 MnO2 + H+ = CO2 + 2 Mn2+ + 3 H2O	85	2.02
•	CH2O + 4 FeOOH + 8 H+ = CO2 + 7 H2O + Fe2+	27	0.64
•	CH2O + 0.5 SO42- + 0.5 H+ = CO2 + 0.5 HS- + H2O	26	0.62
•	CH2O + 0.5 CO2 = CO2 + 0.5 CH4	23	0.55

 The microorganisms offering the oxidation with the highest kJ / mole e- will always win

### Structurally dynamic models (SDMs)







# **Conclusions about ELT:**

 Many observations can be explained by ELT

 Use of SDMs has been successful and build on the validity of SDM

 ELT is in accordance with the observations of the evolution in general and the development ecosystem

## THANK YOU FOR YOUR ATTENTION

