Entropy Production, Polar Ecology and Economics

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Background

- Polar regions have been the subject of human economic activity by outside actors for several hundred years.
- Transportation, whaling, fishing, sealing, fur trapping
- Extraction of coal, hydrocarbons, other mineral resources.
- Substantial effect on the local ecology, and on the economic systems and environment of the countries and regions involved.

To quantify the local and global effects of such activity:

- Advantageous to implement a suitable coupled numerical climatic-biological-economic model.
- Difficulties:
  - large number of parameters and variables
  - poor estimation of model parameters, particularly for earlier historical periods
  - model dynamics may be unstable or very sensitive to uncertainties in the parameters

Nevertheless, some **general principles** may be used to constrain the complex system behaviour

- Ideas from thermodynamics and statistical mechanics:
  - An isolated system *with a large number of degrees of freedom* in thermodynamic equilibrium will tend to a state of ***maximum entropy***, subject to constraints involving the total energy, chemical composition, etc.
  - But an open coupled climate-biological-economic system is in a ***non-equilibrium*** state, favouring maximum ***entropy production*** *(*subject, again, to appropriate constraints).
  - Entropy production corresponds largely with energy consumption (particularly when we consider today's society, based on abundant fossil fuel supplies).

Max. entropy *v.* max. entropy production

Maximum entropy S (isolated system in equilibrium):

$$dS \geq dQ / T \qquad\qquad S = k \log W$$

(Q = heat supplied to system, T = absolute temperature,
k = Boltzmann's constant, W = volume in phase space or number of quantum states with the same macroscopic properties)

Maximum entropy production

A state of maximum rate of entropy production σ was demonstrated to be the most likely state (subject to the relevant constraints) by *Roderick Dewar* (2003):

$$\sigma = \int_V \left[\overline{\boldsymbol{f}_U} \cdot \nabla \left(\frac{1}{T} \right) - \sum_i \overline{\boldsymbol{f}_i} \cdot \nabla \left(\frac{\mu_i}{T} \right) + \frac{1}{T} \sum_{mn} \overline{\phi_{mn} \frac{\partial u_m}{\partial x_n}} - \frac{1}{T} \sum_{ir} \mu_i \nu_{ir} \overline{j_r} \right]$$

integral over domain	heat diffusion	diffusion of matter	mech. energy dissipation	chemical reactions

Diffusion of heat: flux $\boldsymbol{f}_U$ of internal energy U

Diffusion of matter: flux of constituent i with chemical potential μ_i

Eissipation of mechanical energy (stress φ_{mn} × rate of strain $\partial u_m/\partial x_n$

Chemical reactions: reaction rates j_r, stoichiometric coefficients ν_{ir}

Entropy production in a process

If the internal energy changes by δU, the volume by δV, and the quantities of constituents (no. of moles) with chemical potential μ_i by δn_i, the change in entropy δS is given by

$$\delta S = (1/T)\,(\delta U + p\,\delta V - \Sigma_i\,\mu_i\,\delta n_i)$$

More conveniently for processes which take place at or near constant pressure p, we employ the **enthalpy** $H = U + pV$:

$$\delta S = (1/T)\,(\delta H - V\,\delta p - \Sigma_i\,\mu_i\,\delta n_i)$$

How to define a process

- A (dissipative, non-equilibrium thermodynamic) process need not have a fixed volume or occupy a fixed geographical area, provided that:
  - fluxes of matter and energy across the (possibly moving) boundaries can be (reasonably well) defined
  - the exchange of matter and energy with other processes (systems) and the general environment can be specified
- The production of entropy within the process or system can then be defined and distinguished from the flux of entropy through the boundary and from/to other systems
- Thus a process may encompass such concepts as the atmospheric circulation, an organism, or the population of a single species or functional species group (phytoplankton, predators, human populations etc.)

Consequences of entropy production maximisation

- In turbulent flows, structures will appear which will maximise the momentum flux across a turbulent boundary layer (Busse 1970), and convective heat flux
- The population of a species will maximise its use of available nutrients and/or prey, and will evolve to occupy available ecological niches (Darwinian natural selection)
- The economy of a human population will tend to grow, to maximise its use of energy and natural resources, and will develop technology and other cultural devices in order to do so.

Constraints which restrict the rate of entropy production

- Conservation laws for energy, mass, momentum
- The *equations of motion*
- Energy barriers to chemical reaction, leading to slow or zero reaction rates. These may be reduced by *catalysts* (including enzymes etc. in biochemical processes).
- Barriers to species migration, such as too high/low temperature or salinity, and other unfavourable environmental conditions
- For human populations: cultural barriers/taboos, laws and regulations, limited availability of skills or technology

Specific types of (dissipative) process

We may consider the following process types:

- The planetary circulation
- Primary production
- Populations of zooplankton and larger predators
- Human populations and economies

Planetary circulation

Atmospheric and ocean circulation:

- Driven by solar radiation flux (greater at low latitudes)
- Energy loss by long-wave radiation
- Large number of degrees of freedom in (turbulent) circulation
- Maximal entropy production within the atmosphere/ocean, by irreversible heat flux and mechanical energy dissipation
- References: Paltridge 1979, R. D. Lorenz et al. 2001, Ozawa et al. 2001

Planetary circulation

Earth's atmosphere/ocean (based on Lorenz et al. 2001, Ozawa et al. 2001):

- 2-box model (poleward/equatorward of 30°)
- steady-state incoming shortwave radiation, 300 W m^{-2} in tropics, 170 W m^{-2} in polar regions, 120×10^{15} W total
- outgoing longwave radiation by Stefan's law
- max. entropy production occurs with $T = T_0 \sim 300$ K = 27°C in tropics, $T = T_1 \sim 276$ K = 3°C in polar regions
- heat flux between tropics and polar regions $F \sim 32$ W m^{-2}, 8.1×10^{15} W total = 31×10^{-3} W per kg of atmosphere = 0.11 W mol^{-1}
  - considerably smaller rate per kg, mol of ocean, because of greater density
  - compare with $\sim 3\times10^{14}$ W transported northward in the North Atlantic Current (Furevik et al. 2007)
- Entropy production rate
  $\sigma = F(1/T_1 - 1/T_0) \sim 9.4\times10^{-3}$ W m^{-2} K^{-1}, 2.3×10^{12} W K^{-1} total
  = 0.91×10^{-6} W K^{-1} (kg atmosphere)$^{-1}$
  = 31×10^{-6} W K^{-1} (mol atmosphere)$^{-1}$
- Similar computations successfully performed for the planetary circulations of *Mars* and *Titan*

Planetary circulation schematic from Ozawa et al. 2001

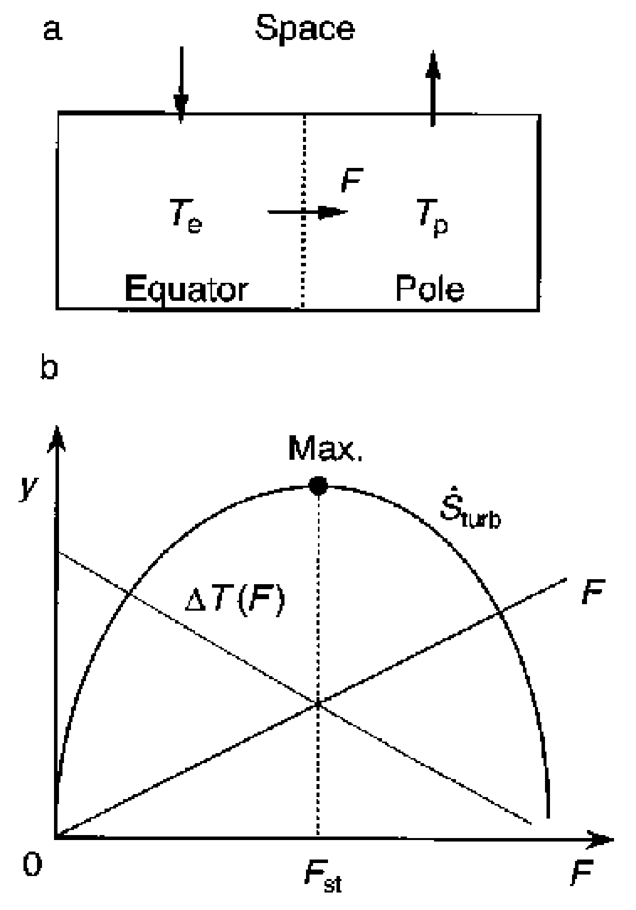


FIG. 6. (a) Schematic illustration of the earth consisting of two regions: equator and pole. F represents the horizontal heat transport by the circulation of the atmosphere and ocean. (b) Corresponding entropy increase rate in the surrounding system due to the heat transport, as a function of F. A maximum exists between the two extreme states: $F=0$ (no circulation) and $\Delta T(F)=0$ (extreme mixing).

Primary production (photosynthesis)

Energy from solar radiation (low-entropy source - blackbody temperature 5800 K)

$$CO_2 + 2H_2O + n_1(h\nu) \rightarrow (1/n_2)(CH_2O)_{n_2} + H_2O + O_2$$

light photons carbohydrate

Energy required:

- $\Delta H \approx$ 470 kJ mol^{-1} : 2-3 photons of visible light per carbon atom are required for the reaction

If the carbohydrate is oxidised in respiration (the reverse reaction, releasing the same amount of energy), the entropy produced at 5°C will be

470/278 ~ 1.7 kJ mol^{-1} K^{-1}

Respiration

- Energy released 470 kJ mol^{-1} ~ 17 MJ / kg carbohydrate ~ 39 MJ / kg C
- Entropy produced at 5°C ~ 1.7 kJ mol^{-1} K^{-1} ~ 63 kJ K^{-1} / kg carbohydrate ~ 140 kJ K^{-1} / kg C

- Production/oxidation of ***lipids***, typical composition $[(CH_2)_{0.9}(CH_2O)_{0.1}]_x$, with x ~ 20, requires/releases more energy, typically 630 kJ / mol C ~ 45 MJ / kg lipid ~ 52 MJ / kg C
- Entropy produced by oxidation of lipids ~ 2.2 kJ mol^{-1} K^{-1} ~ 160 kJ K^{-1} / kg lipid ~ 180 kJ K^{-1} / kg C

Other elements (N, P, Si, S, ...)

- Important/vital for cell biochemistry (particularly N, P!)
- (Non-)availability will act as *constraints* for system
- Analysis of energy/entropy balance/production can be conducted in the same way as photosynthesis/respiration
- Need to account for chemical potential
- Nitrogen fixation analysis requires representation of “microbial loop”
- The “numbers” should usually be much smaller than those encountered in photosynthesis/respiration
- But note that if a necessary nutrient exists at a low concentration, a given mass of it will have a high entropy (increasing as the logarithm of the reciprocal concentration). So the cellular “nutrient pump” will need to generate a similarly large amount of entropy.

Respiration

- Marine phytoplankton in Barents Sea (Sakshaug 1997, we assume ~ 2 × net primary production): 0.13 W m^{-2} ~ 130 W / kg C biomass, entropy prod. at 5°C ~ 0.9 mW K^{-1} m^{-2} ~ 0.49 W K^{-1} / kg C
- Zooplankton (*Calanus*, Vidal 1980):
150 µg individual feeding at 8°C, 9.9% of body carbon respired per day, 0.54 W / mol C, 45 W / kg C, entropy prod. 0.16 W K^{-1} / kg C
- Fish: cod at 2°C, 0.31 W kg^{-1} body mass, entropy prod. 1.1 mW K^{-1} kg^{-1}
- Cetaceans (Brodie 1975), fasting state, 48 W / m^2 body surface, 0.27 W /kg body mass, entropy prod. at 37°C ~ 0.87 mW kg^{-1} K^{-1}

Respiration

– Humans:basal metabolic rate ~100 W, 1.3 W kg^{-1}, entropy prod. at 37°C ~4.2 mW kg^{-1} K^{-1}

– Draught animals (agriculture), horse/cattle, basal metabolic rate ~0.13 W kg^{-1}, entropy prod. ~0.41 mW kg^{-1} K^{-1}

– From G. King (cited in Postan et al. 1941), corn production in late 17th century England was ~1.8×10^6 t, giving an estimated food energy supply of ~1000 MW, ~180 W per individual in the population of 5.5 M, ~2.4 W / kg body mass, entropy prod. 3.2 MW K^{-1} total, 7.8 mW K^{-1} / kg body mass

- This figure includes fodder for livestock and food for persons engaged in heavy manual labour

Energy flow after Welch et al. 1992 in Lancaster Sound marine ecosystem, Arctic Canada

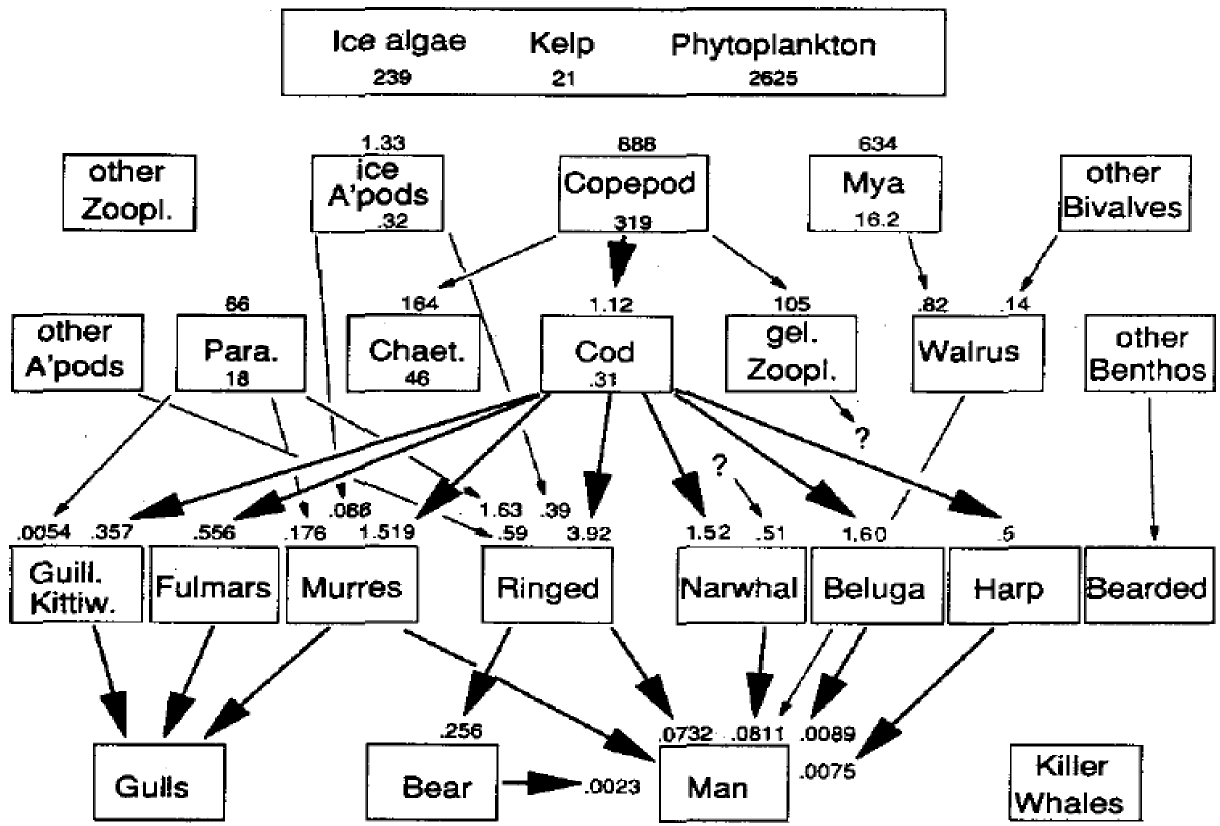
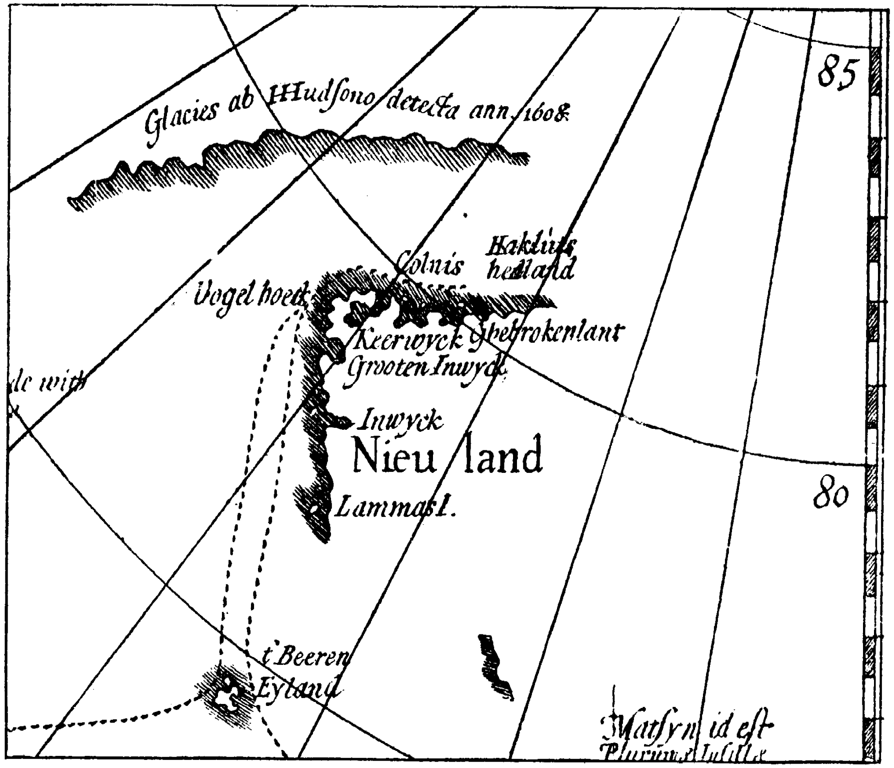


FIG. 9. Energy flow ($kJ \cdot m^{-2} \cdot yr^{-1}$) through parts of the marine food web, Lancaster Sound region (graphic summary of Tables 4, 6 and 7). Numbers at the tops of the boxes are ingestion; numbers inside the boxes are calculated growth; numbers for man are kill rates. Heavy arrows highlight energy flow mediated by arctic cod.



SPITSBERGEN FROM HONDIUS' CHART (1611).

THE MUSCOVY COMPANY'S MAP OF SPITSBERGEN (1625).

Specific example: early whaling activities in Svalbard

- 1600-1700 (Conway 1906)
- Conducted by vessels from England, Netherlands, France, Hamburg, etc.
- Whales initially caught and processed in bays on Spitsbergen
- Later in the period the Dutch (but not the English) processed their catches at sea
- In a good year (1697), 201 ships caught 1968 whales and obtained 63883 casks of blubber (perhaps 13000 tonnes)
- Lipid content corresponds to 570×10^{12} J, spread over the year this is 18 MW, entropy prod. 63 kW K^{-1}

(17th century whaling)

Compare with the size of a “typical” country's economy:

• England 1688 (Gregory King, in Laslett 1971), population 5.5 M, food consumption ~530 MW (plus the consumption by livestock), entropy prod. ~1.9 MW K^{-1}. If we use King's corn production estimates, the total food consumption figure rises to ~1000 MW (entropy prod. ~3.2 MW K^{-1})

• Whale oil was largely used in the making of soap, used to launder fine linen for the elite, thus acting as a “social catalyst” for the political economy

– Elite population of England was about 100k, food consumption ~10-15 MW

– this is of the same order of magnitude as the energy content in the supply of whale lipid to NW Europe

(17th century whaling)

Effect on the marine ecosystem:

- From Sakshaug 1997, new primary production in Barents Sea is 60 g C m^{-2} a^{-1}
- Krill and *Calanus* production is 9.5 g C m^{-2} a^{-1}
- If 5 g of this is available for whales, and they use it with 10% efficiency to produce lipid for “harvesting”, we get 0.58 g lipid m^{-2} a^{-1}
- A production of 13000 tonnes thus requires a primary production area of 22000 km^2
- Was this sustainable? (exercise for the reader)

Discussion/conclusion

- Studies of the energy balance in marine ecosystems are now readily available, particularly since numerical models may now be used in their characterisation
- It should be straightforward to adapt such analyses and models to explicitly account for the entropy production in different parts of the system
- Similarly, accounting for the entropy production in present-day and historical socioeconomic systems should be possible, along the lines of natural resource economics
- I have shown a simple example from the 17th-century Arctic, which may be readily extended in a more precise quantitative manner.

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Supplementary material

Entropy of n moles of an ideal gas (not valid at very low temperatures):

$$S = n\,[\,\text{const.} + c_V \log T + R\,(\log V - \log n)\,]\,,$$

where c_V is the heat capacity at constant volume and R is the gas constant. In terms of concentration $c = n/V$,

$$S = n\,[\,\text{const.} + c_V \log T + R\,\log(1/c)\,]\,,$$

so for a constant mass, the entropy increases as the logarithm of the **reciprocal** concentration.

Similar considerations apply to *dilute aqueous solutions*