Atmospheric composition

Major components

N_2	78%
O_2	21%
Ar	~1%

"Medium" components

CO_2	370 ppmv (rising about 1.5 ppmv/year)
CH_4	1700 ppbv
H_2O	variable

Trace components

H_2	600 ppbv
N_2O	310 ppbv
CO	~100 ppbv
O_3	< 30 ppbv (clean troposphere) ⇒
	82 ppbv (Canadian guideline) ⇒ 300 ppbv
Other hydrocarbons: low ppbv	
NO_x	low pptv-10 ppbv
SO_2	< 1 ppbv

Definitions: ***ppmv and ppbv*** (distinguish from ppm, ppb in solution)

- Unique nature of Earth's atmosphere: O_2 present ⇒ photosynthesis

Regions of the atmosphere and environmental problems

- Troposphere (lower atmosphere, to ~ 15 km)
- Stratosphere (~15-50 km)
- Mesosphere (~50-90 km)
- Thermosphere (> 90 km)

- Most of the mass of the atmosphere (~ 5×10^{15} tonnes) is present in the troposphere (~99% below 30 km)

Tropospheric problems	**Stratospheric problems**
Greenhouse warming	Ozone depletion
Photochemical smog	
Particulates	
Acid precipitation	

Residence times

Definition #1 (kinetics):

$$\tau = 1/\Sigma k'$$

Definition #2 (flows of material)

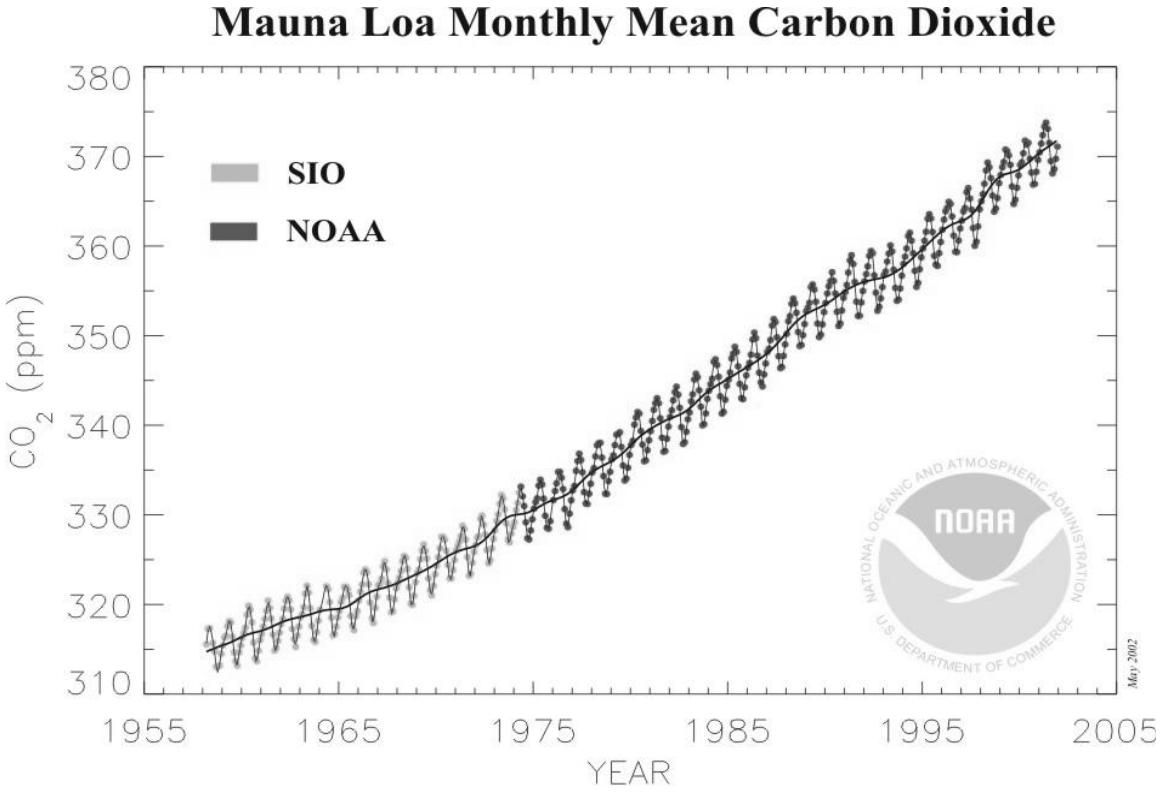
$$\tau = \frac{\text{amount of substance in a “reservoir”}}{\text{rate of inflow to, or outflow from, reservoir}}$$

New terms: ***reservoir; sources; sinks***

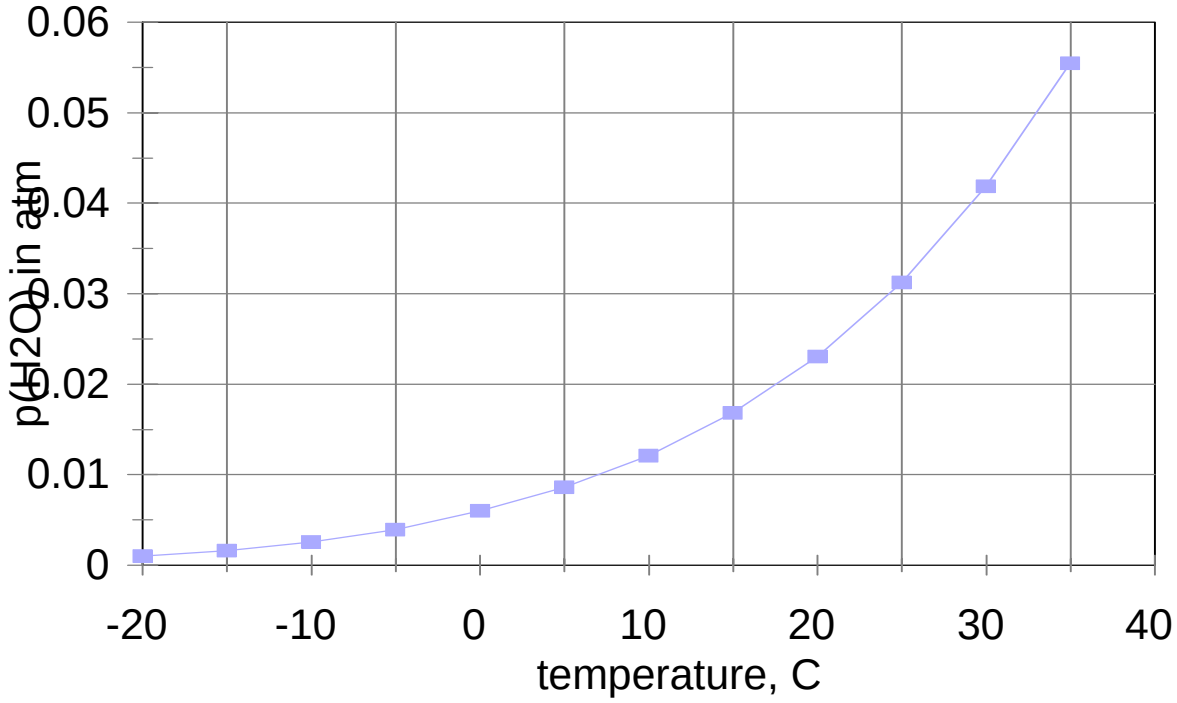
Residence times of atmospheric gases – mostly biologically regulated

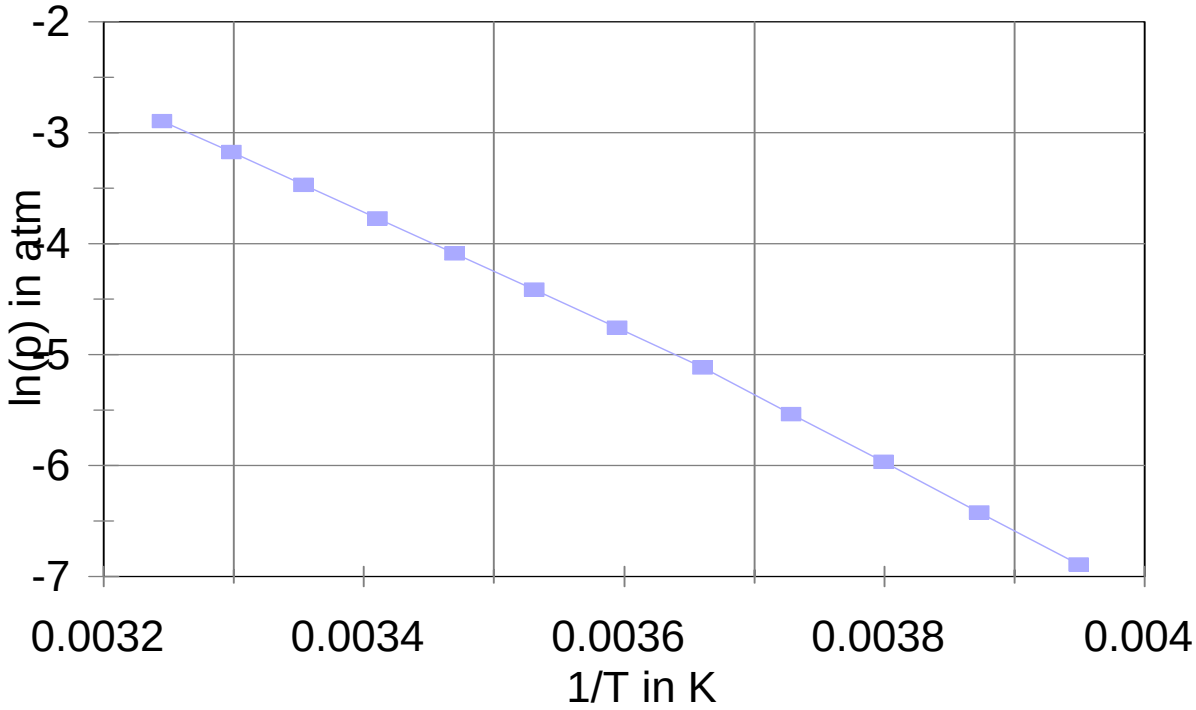
- O_2 $(1.2 \times 10^{15}\ t)/(4.0 \times 10^{11}\ t\ yr^{-1}) = 3.0 \times 10^{3}\ yr$
- N_2 $(3.9 \times 10^{15}\ t)/(3 \times 10^{8}\ t\ yr^{-1}) = 1 \times 10^{7}\ yr$
- CO_2 $(6.2 \times 10^{11}\ t)/(3.7 \times 10^{11}\ t\ yr^{-1}) = 1.7\ yr$

  rate of increase 1.5 ppmv/yr



- H_2O $(1.3 \times 10^{10}\ t)/(4.3 \times 10^{11}\ t\ yr^{-1}) = 3.0 \times 10^{-2}\ yr$ (10 d)


0.06
0.05
0.04
0.03
0.02
0.01
0
p(H2O) in atm
-20
-10
0
10
20
30
40
temperature, C


-2
-3
-4
-5
-6
-7
ln(p) in atm
0.0032
0.0034
0.0036
0.0038
0.004
1/T in K

Vapour pressure of water as *f*(temperature)

Solar energy and photochemical reactions

- Photochemical reactions are caused or accelerated by light

- Sunlight can supply the energy to drive chemical reactions that would otherwise be unfavourable energetically

- Absorption of light raises the substrate to an "excited" state

- Photochemical reactions require prior absorption of photons: 1 photon absorbed per atom or molecule)

$$E_{photon} = hc/\lambda \quad (E \text{ inversely proportional to } \lambda)$$

Multiply by Avogadro's Constant to get the energy per mole

$$\Delta E, \text{ kJ mol}^{-1} = (1.19 \times 10^5)/\lambda, \text{ nm}$$

***Example**: Calculate the energy of (i) one photon of wavelength 530 nm; (ii) a mole of photons of wavelength 530 nm. [*Answers:* 3.7×10^{-19} J; 225 kJ mol^{-1}]

Ranges of radiation

visible	400(blue) to 700(red) nm
UV-A	400-325 nm
UV-B	325-295 nm (limit of λ reaching the surface)
UV-C	< 295 nm (present in upper atmosphere)

Energy vs. Wavelength of UV and visible radiation

Wavelength, nm	Energy, kJ mol^{-1}
700	170
500	240
400	300
300	400

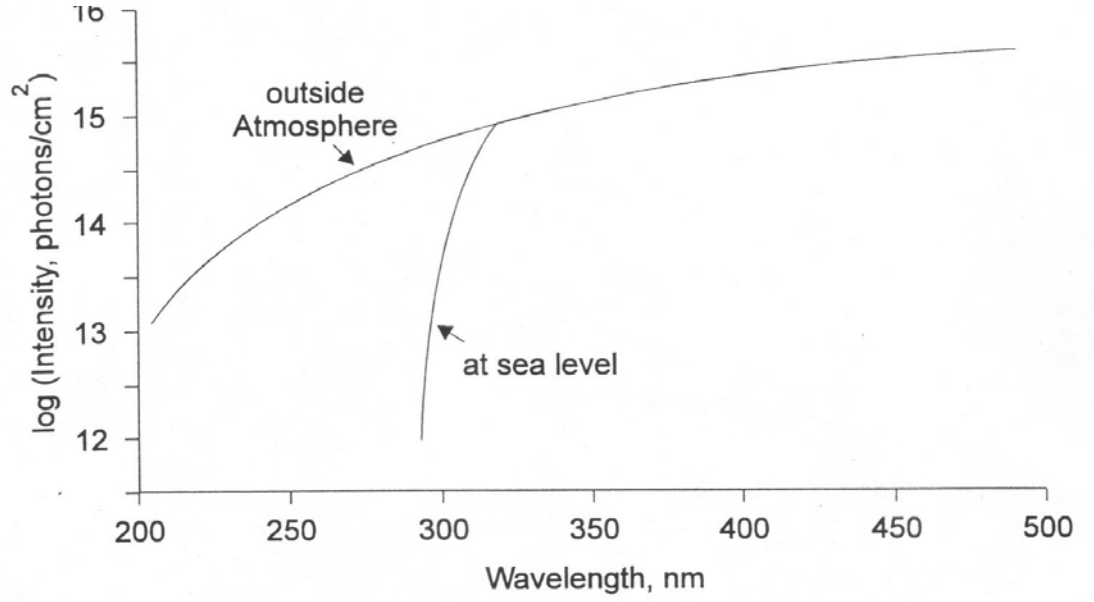
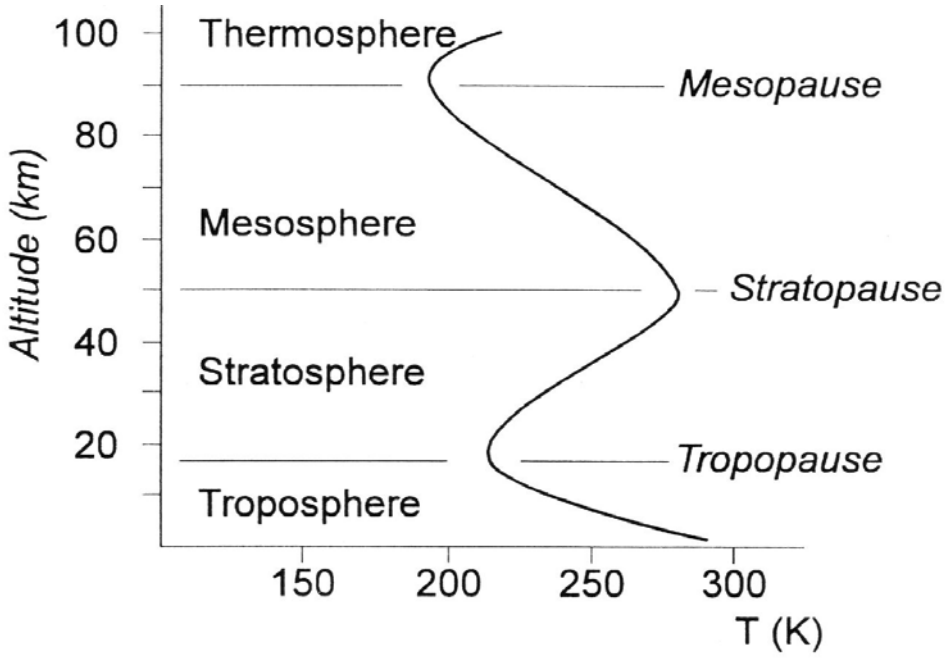


Table: Some common bond strengths, kJ mol^{-1}

O=O	495	N≡N	946
C=C	620	C-C	350
O-H water	490	O-H (typical)	464
C-Cl	330	Cl-Cl	243
C-H (typical)	414 (range ~380-460)		

***Example**: The C-Cl bond has bond dissociation energy 330 kJ mol^{-1}, while $CFCl_3$ absorbs radiation having $\lambda < 220$ nm. Will $CFCl_3$ undergo bond cleavage in the lower atmosphere? [*Answer:* 330 kJ mol^{-1} corresponds to $\lambda = 360$ nm, but .....]

Temperature profile of the atmosphere: the importance of sunlight (= photochemistry)



- Thermosphere, mesosphere: radiation < 200 nm is absorbed

  $N_2 \rightarrow 2N$ and $N_2 \rightarrow N_2^+ + e^-$

  followed by recombination

- Stratosphere: radiation 200-300 nm is absorbed by O_2

  $O_2 \rightarrow \rightarrow O_3$

  followed by $O_3 \rightarrow \rightarrow O_2$

- These processes convert solar radiation (light) into heat

- Radiation > 300 nm reaches the Earth's surface

- The lowest part of the troposphere is warm because the Earth radiates infrared radiation which is trapped by the atmosphere

Greenhouse gases and climate change

- Greenhouse effect = trapping of *outgoing* infrared radiation by "radiatively active gases"
- Physical chemistry: infrared radiation always accompanied by a change of dipole moment in the lower and upper vibrational states
- Above rule means that the following do NOT absorb IR:
  N_2; O_2; Ar These are the major constituents of the atmosphere
- ***Conclusion***: Trace gases are responsible for IR absorption <u>in the troposphere</u>
  H_2O; CO_2; O_3; CH_4; N_2O; CFCs (chlorofluorocarbons)

- Without IR absorption the average surface temperature of Earth would be ~ −30˚C rather than ~ +15˚C
- "Greenhouse effect" as commonly understood means <u>increased</u> IR trapping due to increases in the concentrations of CO_2; CH_4; N_2O; CFCs —> warming of the troposphere
- Potential positive feedback from H_2O if temperature increases

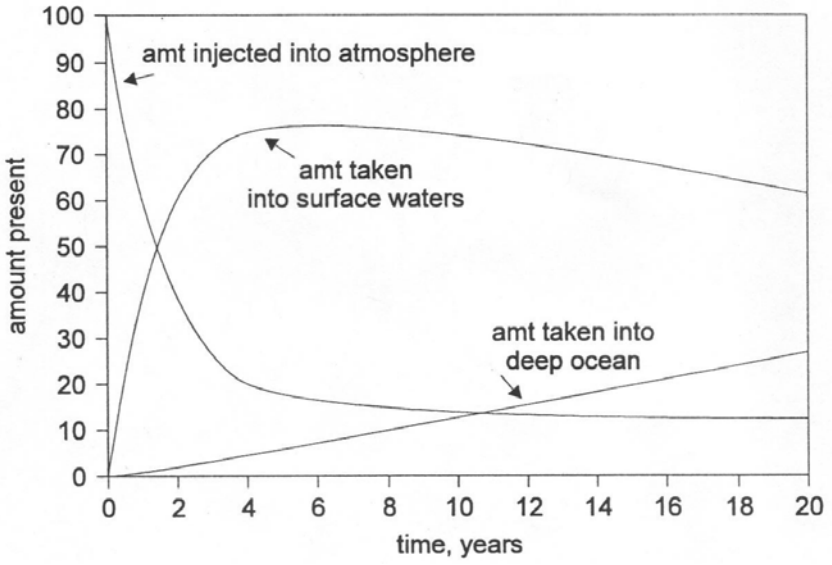
• CO_2	CH_4	N_2O	CFCs
Present Levels			
370 ppmv	1750 ppbv	310 ppbv	high pptv
Atmospheric Lifetimes (years; vary with individual CFC)			
1.7	12	114	60-150
Global Warming Potentials (per tonne; vary with individual CFC)			
1	11	270	> 3000

CO_2: atmosphere and ocean

$CO_2(g) \rightleftharpoons CO_2(aq) \equiv H_2CO_3(aq) \rightleftharpoons HCO_3^-(aq) \rightleftharpoons CO_3^{2-}(aq) \rightleftharpoons CaCO_3(s)$

Issues:

1. How fast will the oceans take up injections of CO_2 into the atmosphere? $t_{½}$ for uptake into surface water = 1.3 years, for exchange between surface and deep water $t_{½}$ = 35 years



2. What would be the effect of an increase in water temperature?

   $CO_2(aq)$ —> $CO_2(g)$ equilibrium constant K_H increases with T, hence possibility of positive feedback

Is global warming a fact?
If so, is it due to increased concentrations of greenhouse gases?
If so, are human activities to blame?
[Figures from 2001 Report of the International Panel on Climate Change]

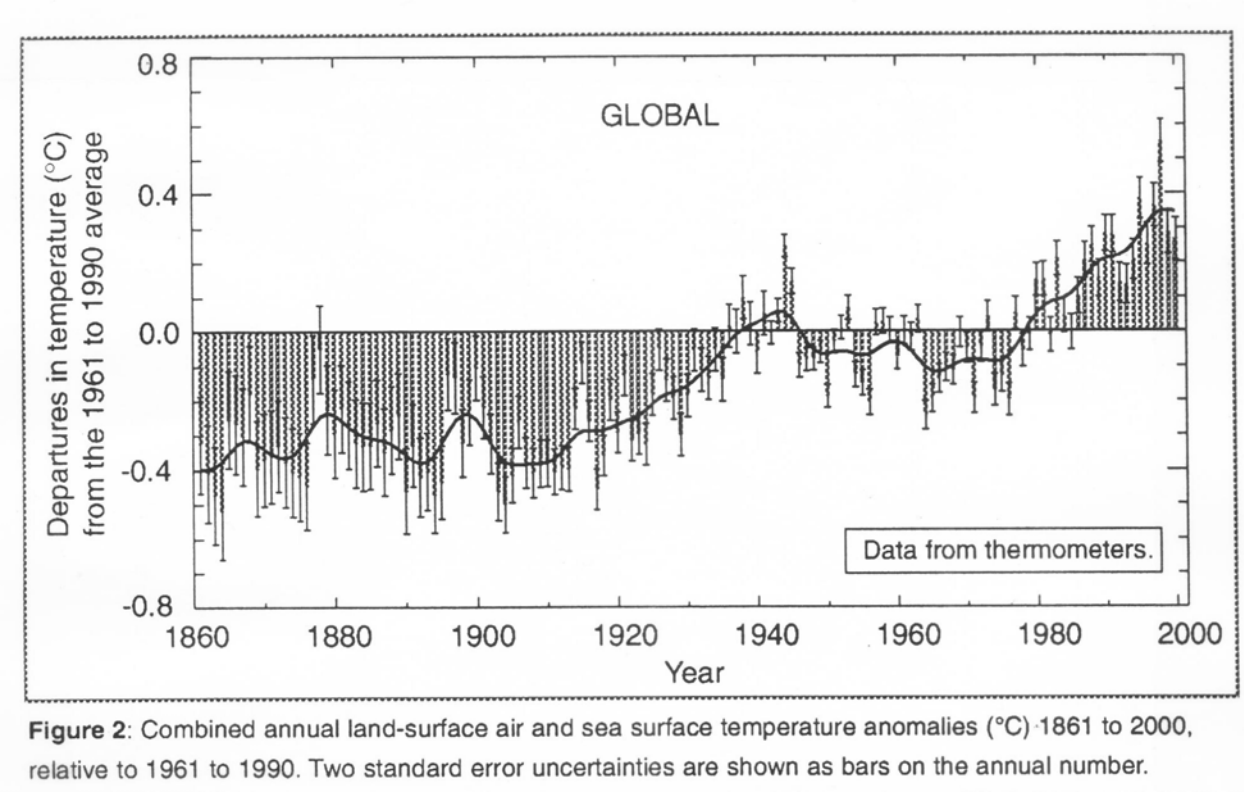
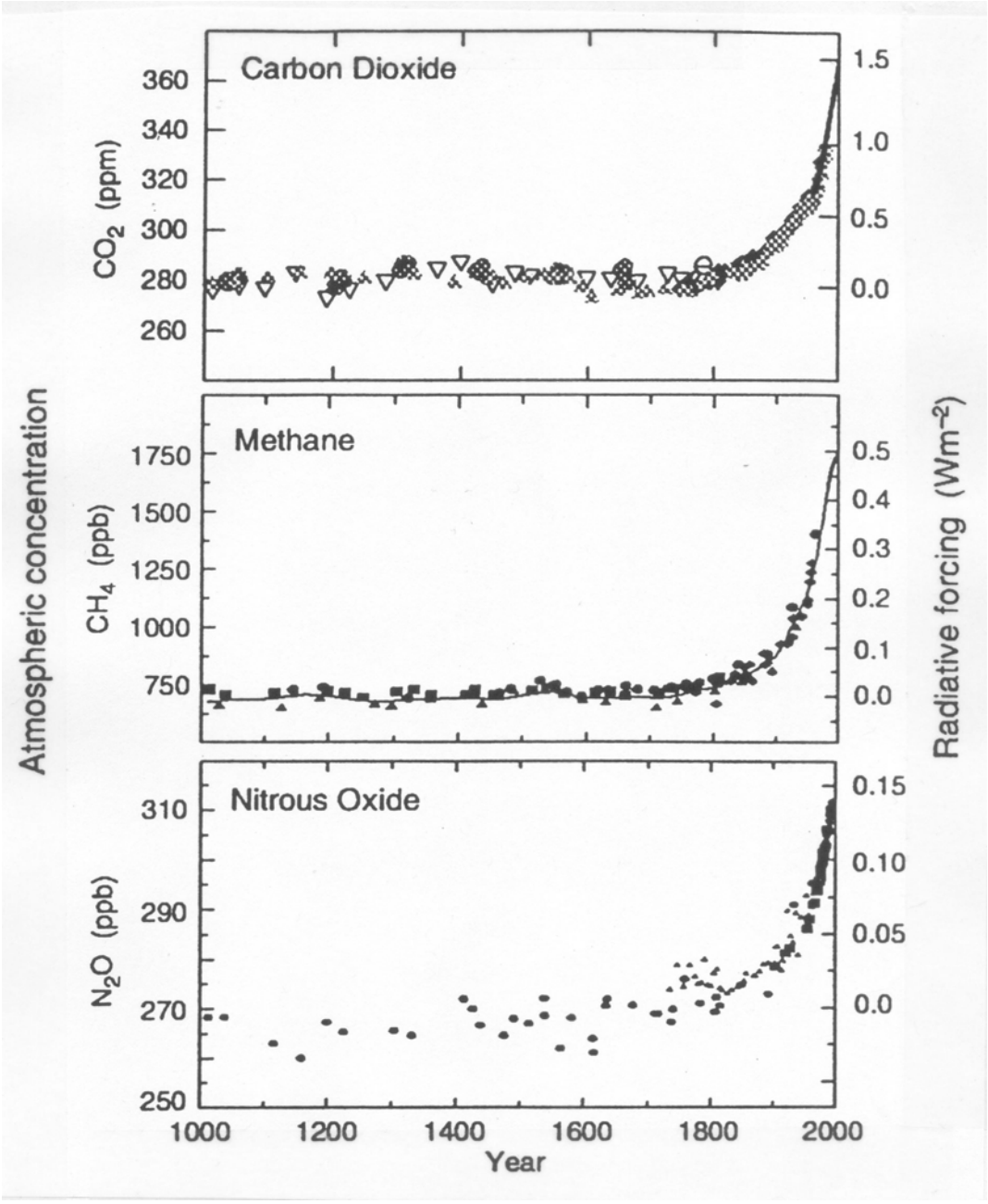


Figure 2: Combined annual land-surface air and sea surface temperature anomalies (°C) 1861 to 2000, relative to 1961 to 1990. Two standard error uncertainties are shown as bars on the annual number.

Historic Increases of CO_2, CH_4, and N_2O [IPCC Report]

Data are from ice cores in Antarctica and Greenland, supplemented in recent years by direct atmospheric analysis



What is the Kyoto Agreement?

- International agreement reached in 1990 for developed countries to cut back their CO_2 emissions by 6% from their 1990 levels
- The 2001 IPCC Report suggests that temperature increases of >3˚C are likely before 2100; this would greatly change the climate in many regions
- Controversies: easier for some countries than others, depending on their "energy mix"
- Not all (but most!!!) commentators agree that human activities are to blame
- Even if the cause is human activities, there is little point in only some countries meeting their targets
- Canada is a huge fossil fuel user per capita, but does not contribute a high percentage of the world's total CO_2 budget
- Canada, like most other countries, will not impose a carbon tax
- Canada is arguing for carbon credits for agriculture and reforestation
- Quebec is on a collision course with Alberta, because Alberta is a source of fossil fuels, whereas Quebec generates a lot of hydroelectricity

What should be done?

- Immediately reduce emissions of greenhouse gases?
- Adjust to changed climatic conditions?

Stabilization of Atmospheric CO_2 Levels [IPCC Report]

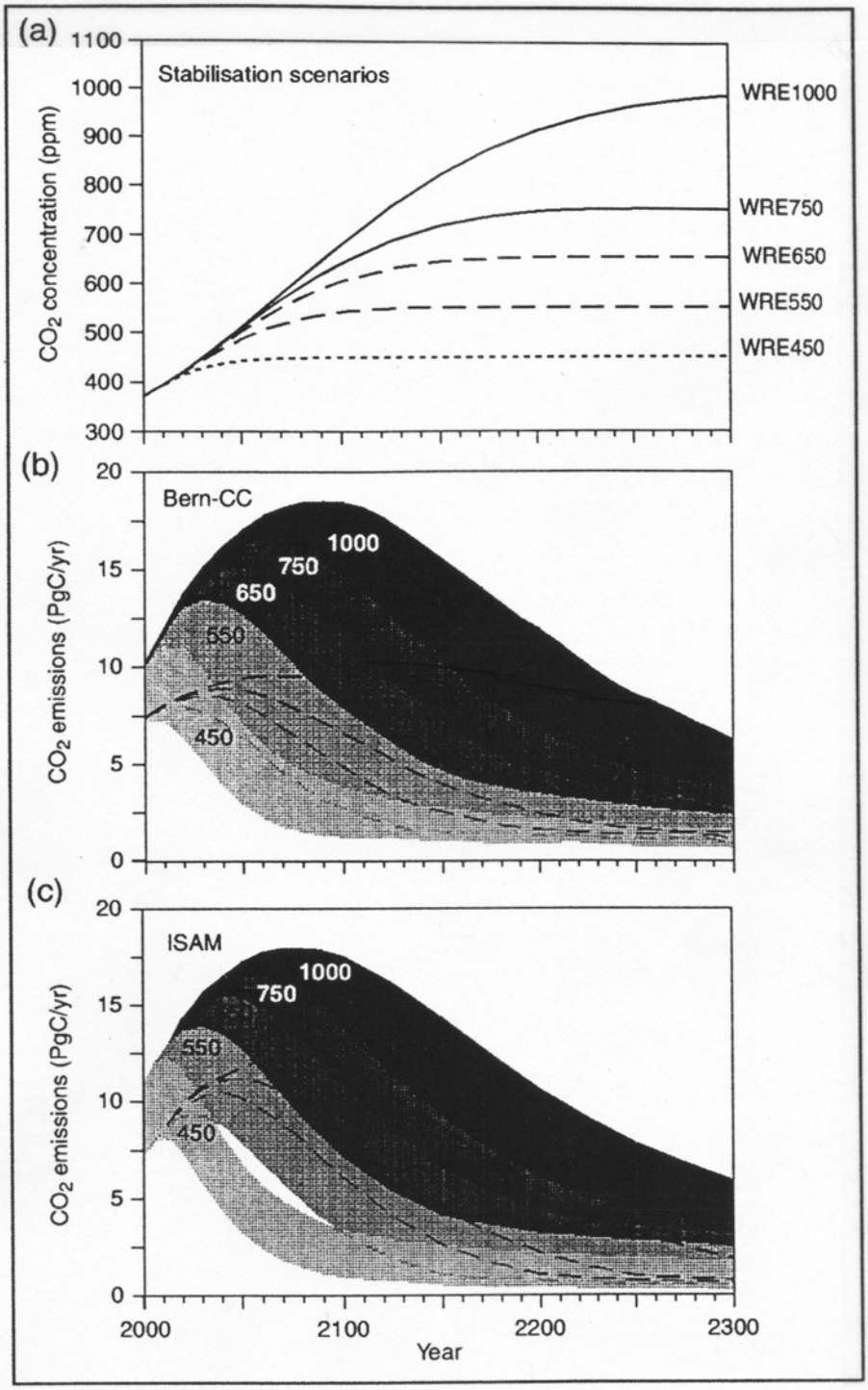


Figure 25: Projcted CO_2 emissions permitting stabilisation of atmospheric CO_2 concentrations at different final values. Panel (a) shows the assumed trajectories of CO_2 concentration (WRE scenarios) and panels (b) and (c) show the implied CO_2 emissions, as projected with two fast carbon cycle models, Bern-CC and ISAM.

Predicted Changes in Global Temperatures

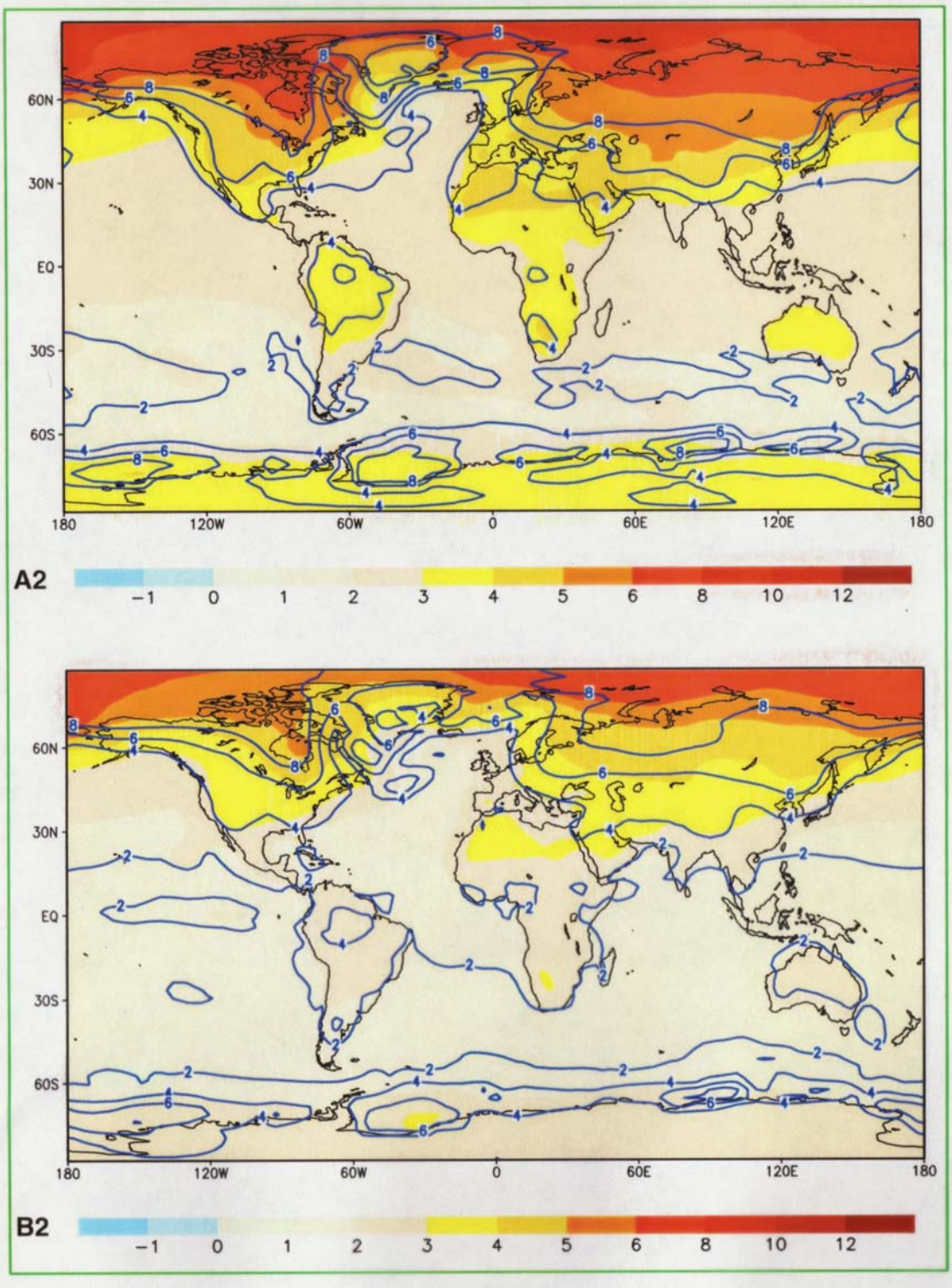


Figure 20: The annual mean change of the temperature (colour shading) and its range (isolines) (Unit: °C) for the SRES scenario A2 (upper panel) and the SRES scenario B2 (lower panel). Both SRES scenarios show the period 2071 to 2100 relative to the period 1961 to 1990 and were performed by OAGCMs. [Based on Figures 9.10d and 9.10e]

Global Precipitation Map

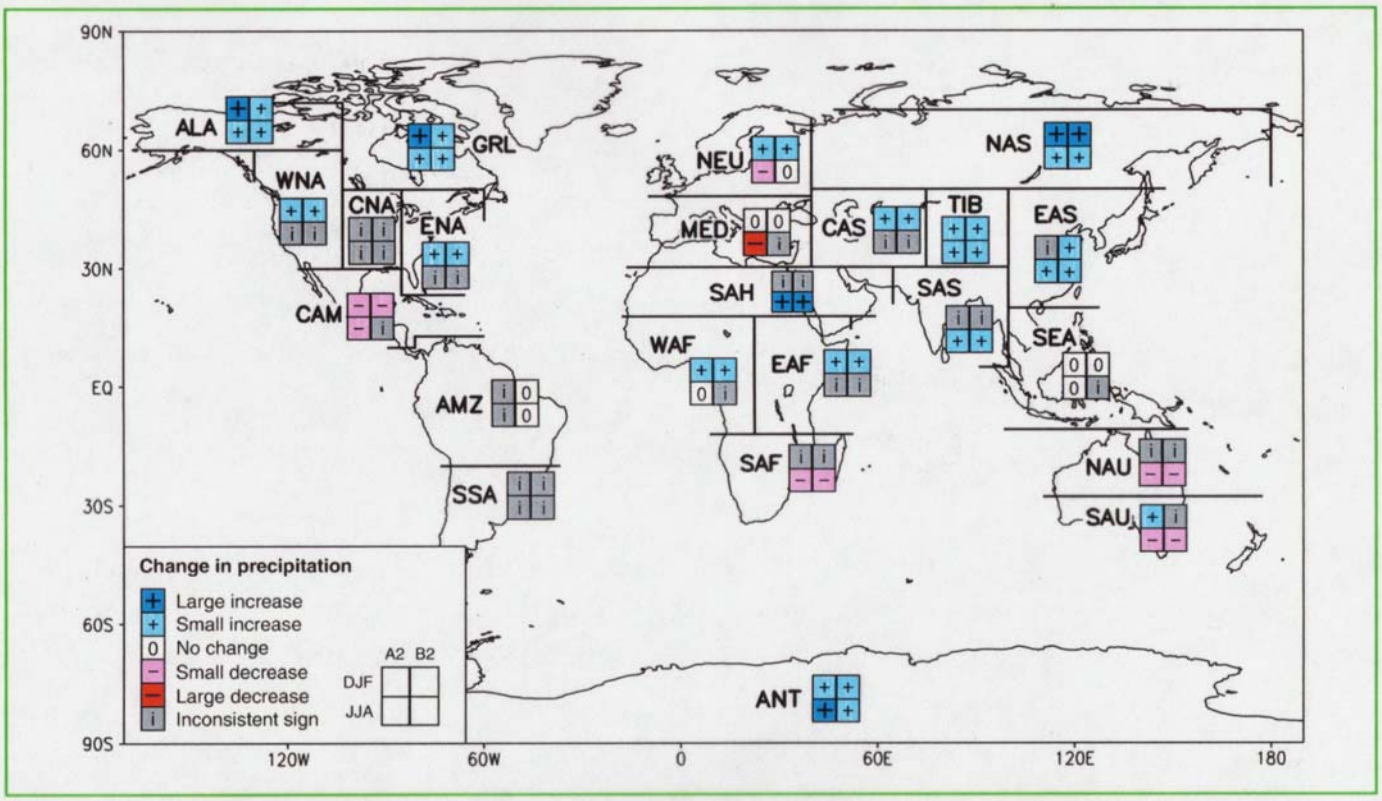


Figure 23: Analysis of inter-model consistency in regional precipitation change. Regions are classified as showing either agreement on increase with an average change of greater than 20% ('Large increase'), agreement on increase with an average change between 5 and 20% ('Small increase'), agreement on a change between –5 and +5% or agreement with an average change between –5 and 5% ('No change'), agreement on decrease with an average change between –5 and –20% ('Small decrease'), agreement on decrease with an average change of less than –20% ('Large decrease'), or disagreement ('Inconsistent sign'). A consistent result from at least seven of the nine models is deemed necessary for agreement. [Based on Chapter 10, Box 1, Figure 2]

Predicted Sea Level Rise

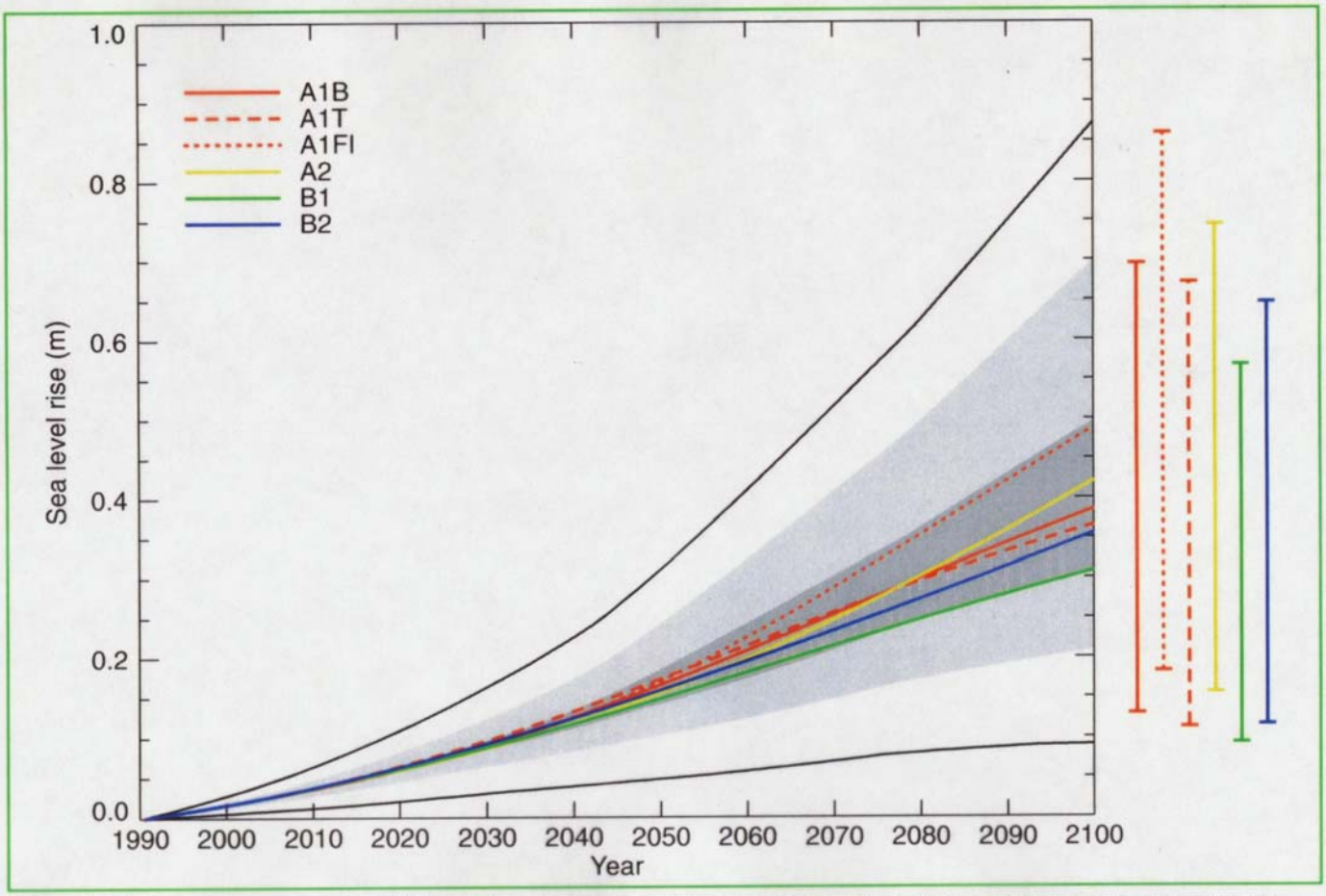


Figure 24: Global average sea level rise 1990 to 2100 for the SRES scenarios. Thermal expansion and land ice changes were calculated using a simple climate model calibrated separately for each of seven AOGCMs, and contributions from changes in permafrost, the effect of sediment deposition and the long-term adjustment of the ice sheets to past climate change were added. Each of the six lines appearing in the key is the average of AOGCMs for one of the six illustrative scenarios. The region in dark shading shows the range of the average of AOGCMs for all thirty five SRES scenarios. The region in light shading shows the range of all AOGCMs for all thirty five scenarios. The region delimited by the outermost lines shows the range of all AOGCMs and scenarios including uncertainty in land-ice changes, permafrost changes and sediment deposition. Note