

# Air Pollution Control and Air Chemistry:

Introduction to fundamental processes in the atmosphere  
(1<sup>st</sup> lecture)

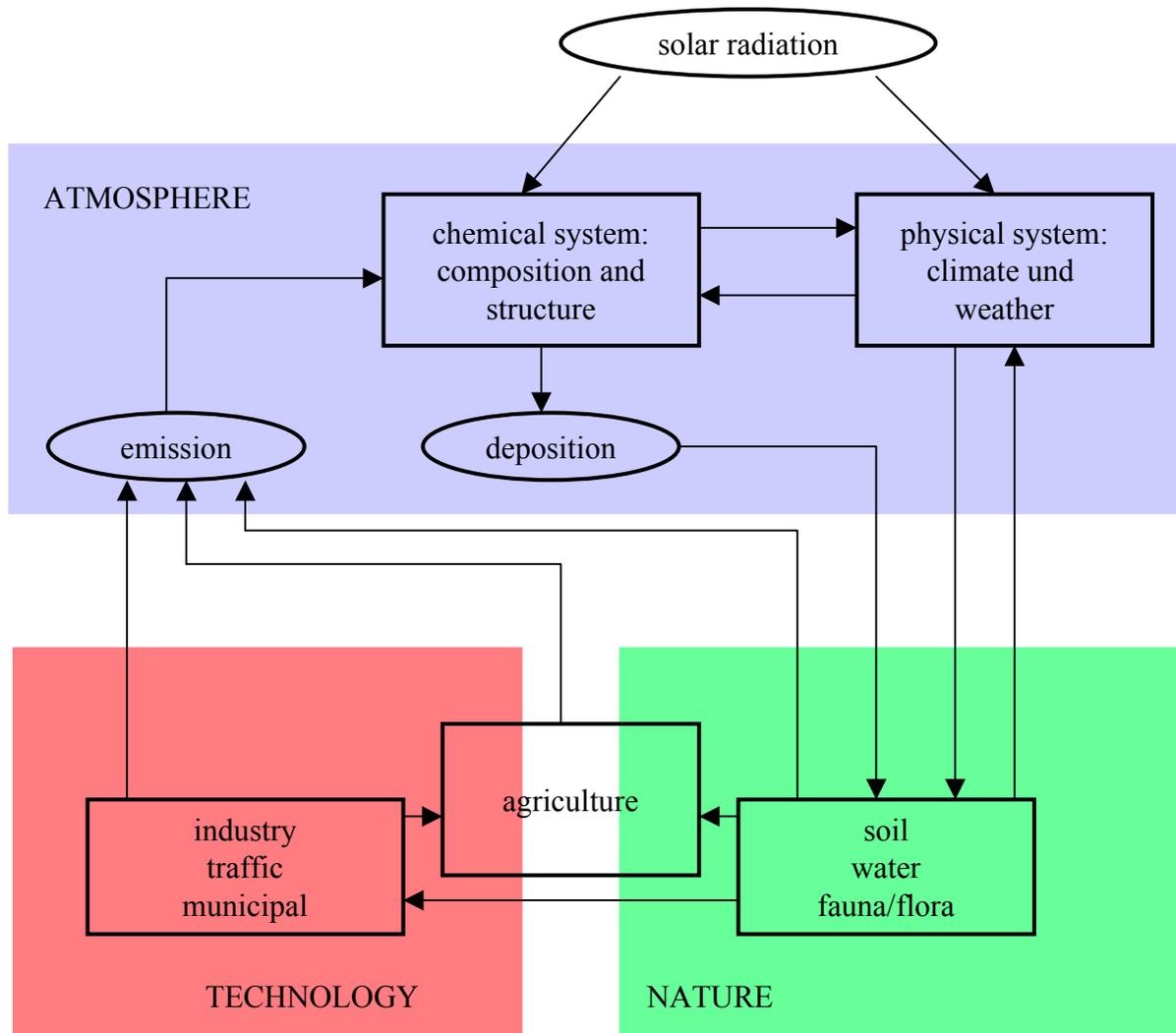
Detlev Möller

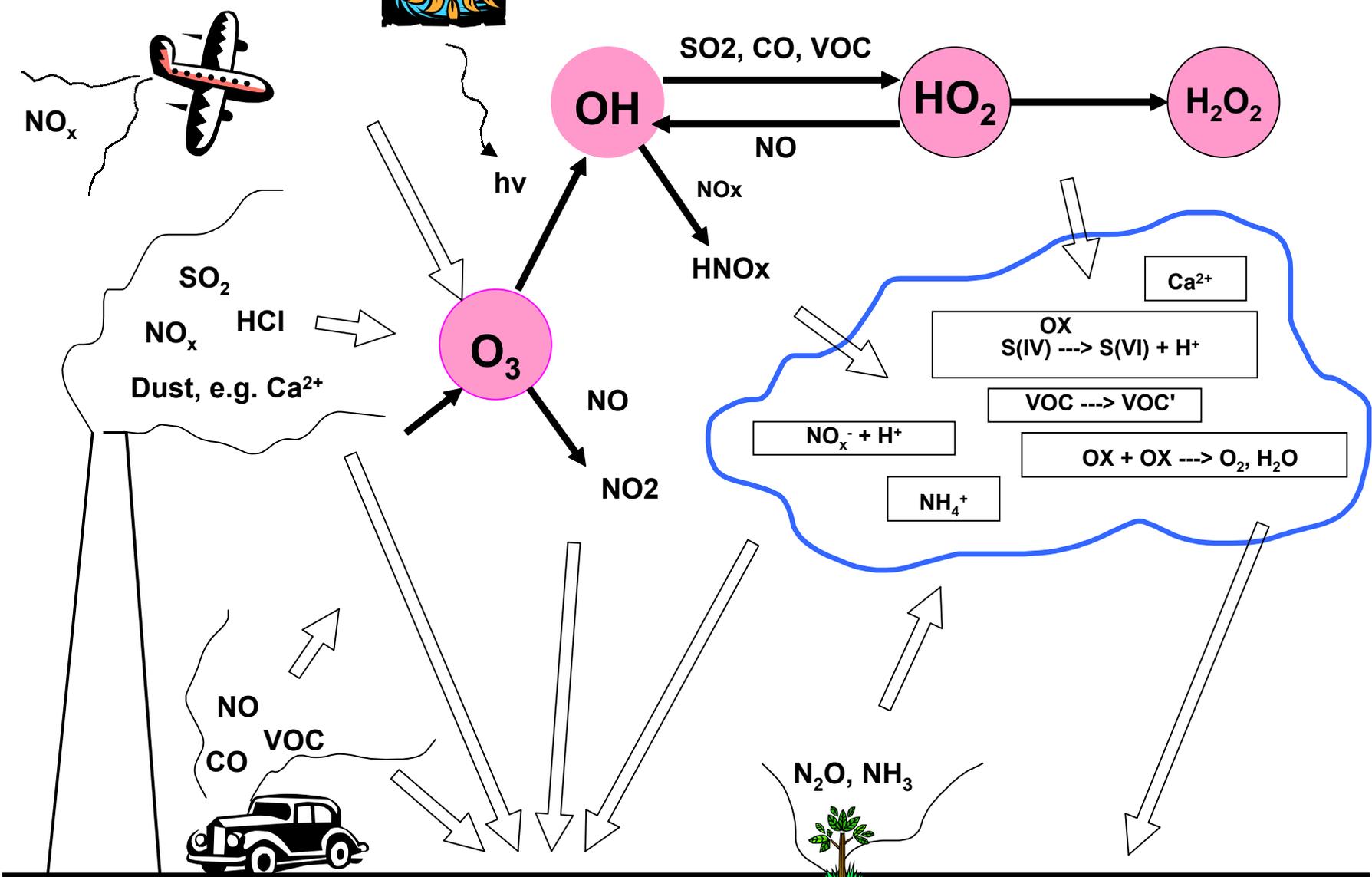
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# Objectives:

To describe the atmosphere as a chemical and physical system, controlled by solar radiation, terrestrial natural (biogenic and geogenic) processes as well anthropogenic activities.

- The atmosphere
- Air composition and problems
- Air pollution
- The climate system





$\text{NO}_x$



$h\nu$

**OH**

$\text{SO}_2, \text{CO}, \text{VOC}$

**HO<sub>2</sub>**

**H<sub>2</sub>O<sub>2</sub>**

$\text{NO}$

$\text{NO}_x$

$\text{HNO}_x$

$\text{SO}_2$

$\text{NO}_x$

$\text{HCl}$

**O<sub>3</sub>**

$\text{NO}$

$\text{NO}_2$

Dust, e.g.  $\text{Ca}^{2+}$

$\text{Ca}^{2+}$

$\text{OX}$   
 $\text{S(IV)} \rightarrow \text{S(VI)} + \text{H}^+$

$\text{VOC} \rightarrow \text{VOC}'$

$\text{NO}_x^- + \text{H}^+$

$\text{OX} + \text{OX} \rightarrow \text{O}_2, \text{H}_2\text{O}$

$\text{NH}_4^+$

$\text{NO}$

$\text{CO}$

$\text{VOC}$



$\text{N}_2\text{O}, \text{NH}_3$



Industrial & urban emission

dry deposition

agricultural emission

wet deposition

## Definitions & statements

**Air** = chemical multiphase system consisting from gaseous species, particulate matter and droplets (= chemical system of the lower atmosphere. i.e. until the meso pause)

**Atmosphere** = reservoir surrounding the earth surface; including the high atmosphere where air is not longer defined

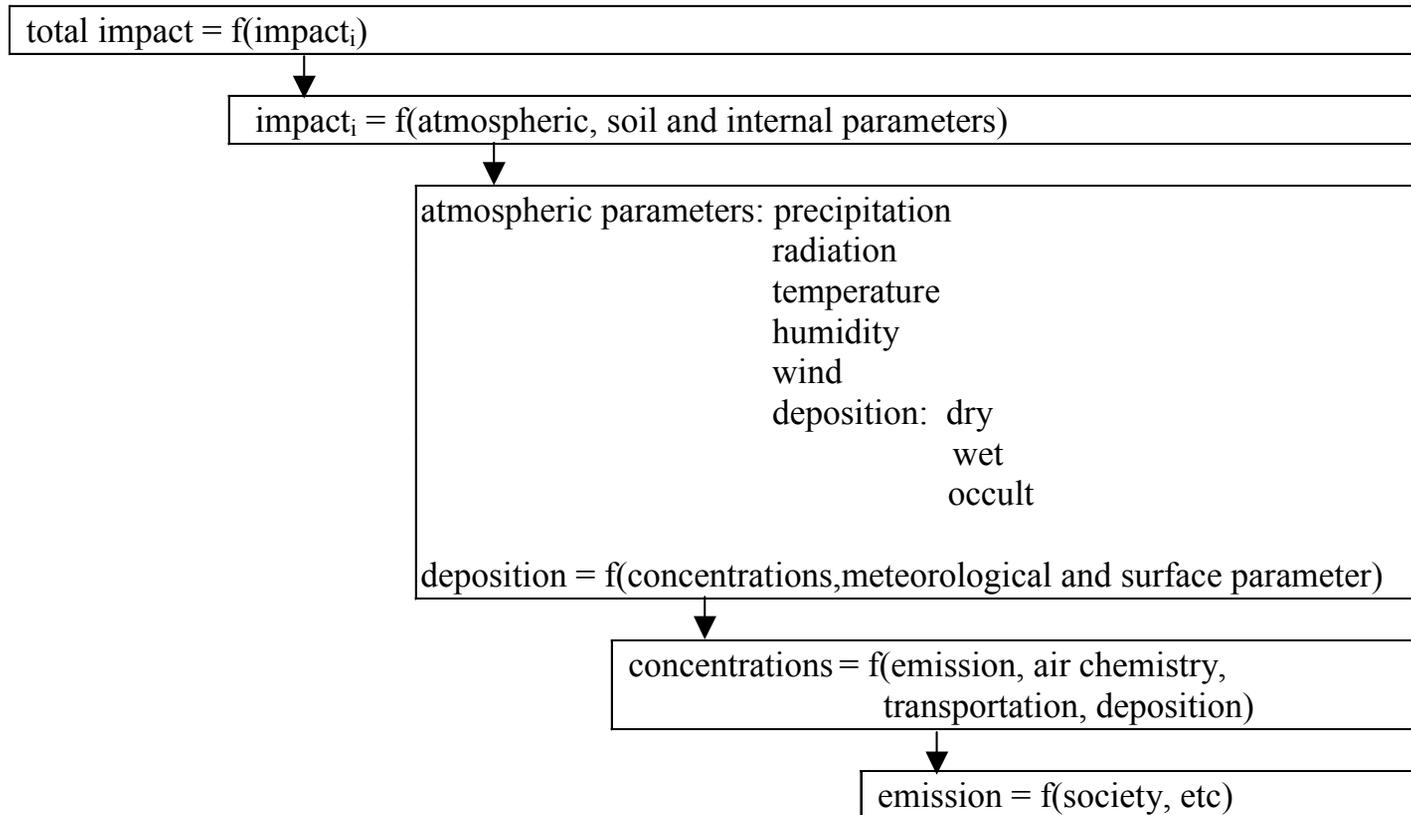
The chemical composition of the atmosphere (i.e. “**Air Chemistry**”) is a result of emissions into the atmosphere, chemical reactions (transformation), transport processes (mixing) and energetic processes (“**Physics of the Atmosphere**”). The **natural** air chemistry is a result of the evolution of the biosphere-atmosphere interaction.

Man-made activities lead to a *changing chemical composition* of the atmosphere, which is called **Air Pollution**, i.e.,  $X_{\text{present}} - X_{\text{natural}} = X_{\text{pollutant}}$

An **Effect** is a results of an **Impact**, which, however, is given by the total concentration ( $X_{\text{natural}} + X_{\text{pollutant}}$ ). Therefore, impact assessment needs a separation between natural and man-made influences suggesting abatement strategies. Co-impacts (external and internal) must be considered. Effects only occur when the impact exceeds a threshold.

# The impact to an ecosystem is a system of hiercharchic functional relationships

*(Deposition as an example for atmospheric parameter):*



*example for feedback relations:*

air chemistry depends from the ecosystem (i.e. the impact itself) in sense of emission and deposition fluxes

*Air chemistry is defined ... as the branch of atmospheric science concerned with the constituents and chemical processes of the atmosphere ...* (Christian Junge, 1963)

A **clean atmosphere** is a political target, i.e., an air chemical composition (defined in time and scale) which should provide a sustainable development.

The **natural atmosphere** does not longer exist; it was the air chemical composition without man-made influence. However, the definition is not exactly because humans are part of the **nature**...

On the other hand, humans – by decoupling of her life cycle from only natural conditions – have altered „natural“ biogeochemical cycles. *Vernadsky* understood with **noosphere** a new dimension of the biosphere, developing under the evolutionary influence of humans on natural processes.

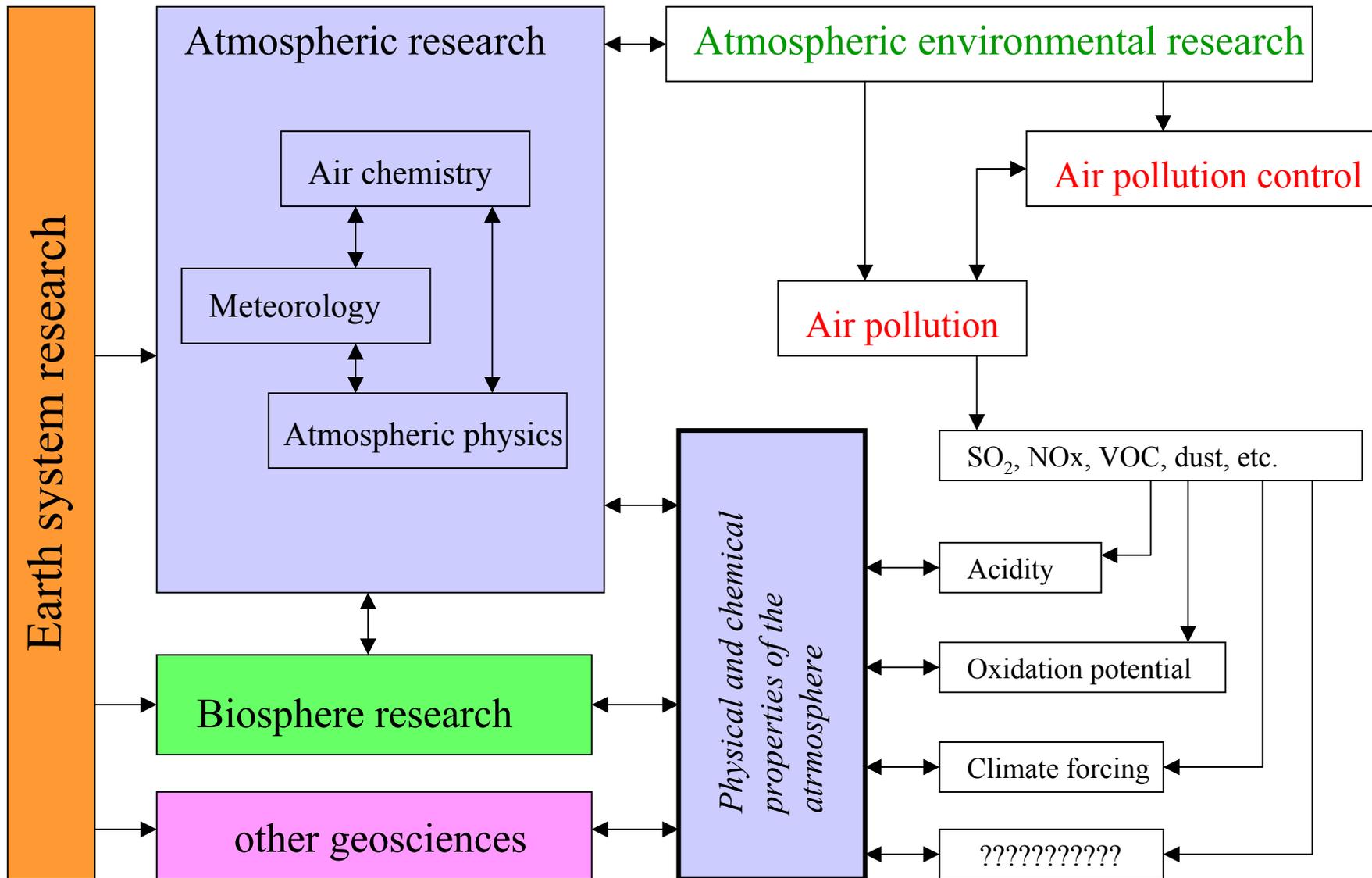
composition of the dry remote atmosphere  
(global mean concentrations)

substituent		concentration (in ppm $\equiv 10^{-4}$ %)	remarek
nitrogen	N <sub>2</sub>	780840 <sup>a</sup>	constant
oxygen	O <sub>2</sub>	209460 <sup>a</sup>	constant
argon	Ar	9340 <sup>a</sup>	constant
carbon dioxide	CO <sub>2</sub>	360	increasing
neon	Ne	18,18	constant
helium	He	5,24	constant
methane	CH <sub>4</sub>	1,73	increasing
krypton	Kr	1,14	constant
hydrogen	H <sub>2</sub>	0,5	constant
dinitrogen monoxid	N <sub>2</sub> O	0,31	steigend
carbon monoxid	CO	0,120	increasing
xenon	Xe	0,087	constant
ozone	O <sub>3</sub>	0,03	variabel
carbonylsulfid	CSO	0,00066	increasing
nitric acid <sup>b</sup>	HNO <sub>3</sub>	$\leq 0,001$	variable
radikals <sup>c</sup>		$< 0,00001$	variable
hydroxyl radikal	OH	0,0000003	variable

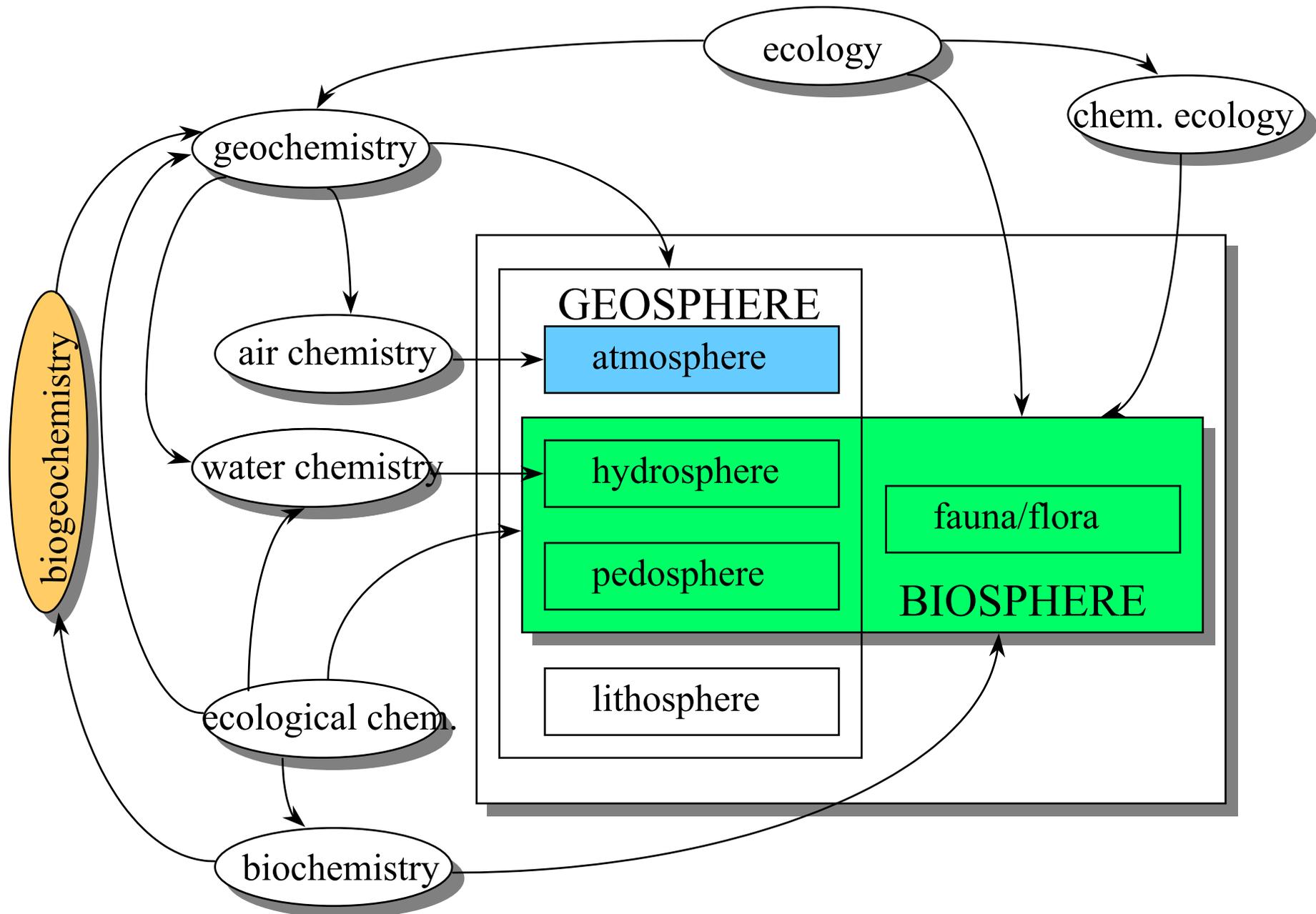
<sup>a</sup> related to the “clean” atmosphere O<sub>2</sub> + N<sub>2</sub> + Ar + CO<sub>2</sub>

<sup>b</sup> and many other trace substances (NH<sub>3</sub>, NO<sub>x</sub>, HCl, NMHC, H<sub>2</sub>O<sub>2</sub>, DMS, CFC’s et. al.)

<sup>c</sup> e.g. HO<sub>2</sub>, NO<sub>3</sub>, Cl



# CHEMICAL ENVIRONMENTAL RESEARCH



# Chemistry and physics being sciences of „observing“ the environment (our “senses”)

„extern“ disciplins		information interface „human“ ↓	„intern“ disciplin  ↓
<i>Chemistry</i> →	<i>Substances</i>	smell	→ <i>Biology</i>
		taste	
↑ <i>Physics</i> →	<i>Optics</i>	seeing	
	<i>Akustics</i>	hear	
	<i>Thermodynamics</i>	feel	
	<i>Mechanics</i>	touch	

# Problems in spatial scale

local

dust

local → regional

SO<sub>2</sub>, aerosol

local → global

CO<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub>O

local → regional → global

O<sub>3</sub>

space<sub>1</sub> → space<sub>2</sub>

„acid rain“

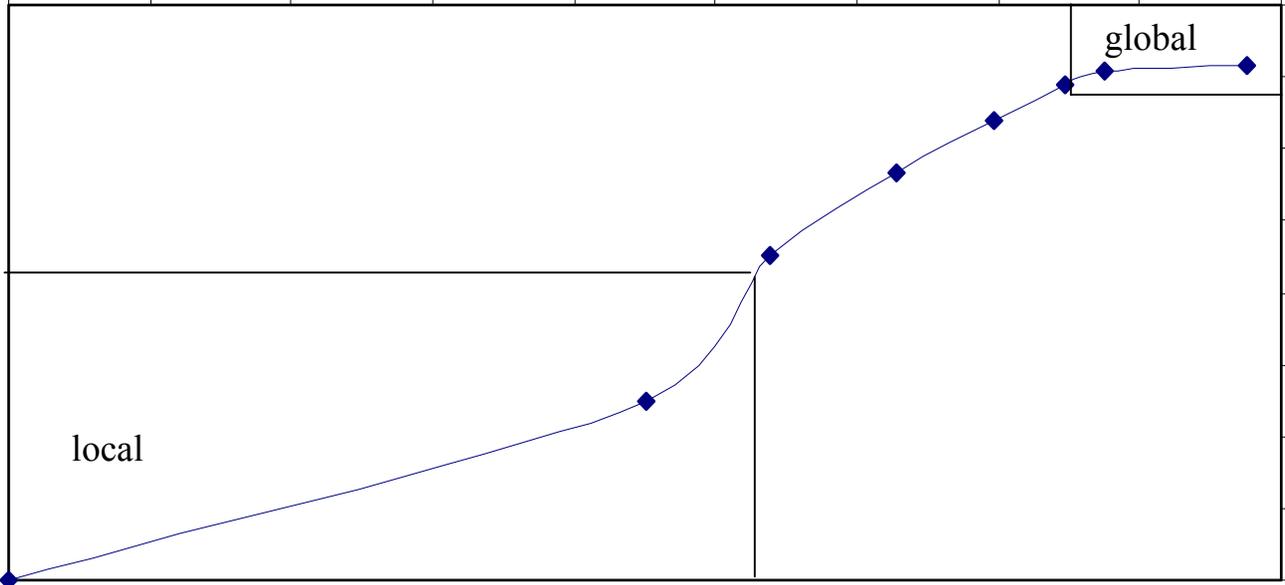
# Atmospheric problems in temporal scale

Positive climate forcing (greenhouse effect)	100 years
Background ozone	50 years
Negative climate forcing (aerosol)	2 weeks
Sommermog	1 week
Wintersmog	1 week
Disaster	1 day

← shorter 1 s 1 d 1 a longer →

time (s)

1,00E-09 1,00E-07 1,00E-05 1,00E-03 1,00E-01 1,00E+01 1,00E+03 1,00E+05 1,00E+07 1,00E+09



distance (km)

local

global

chem. elementary reactions

dissipation eddies

turbulence

clouds

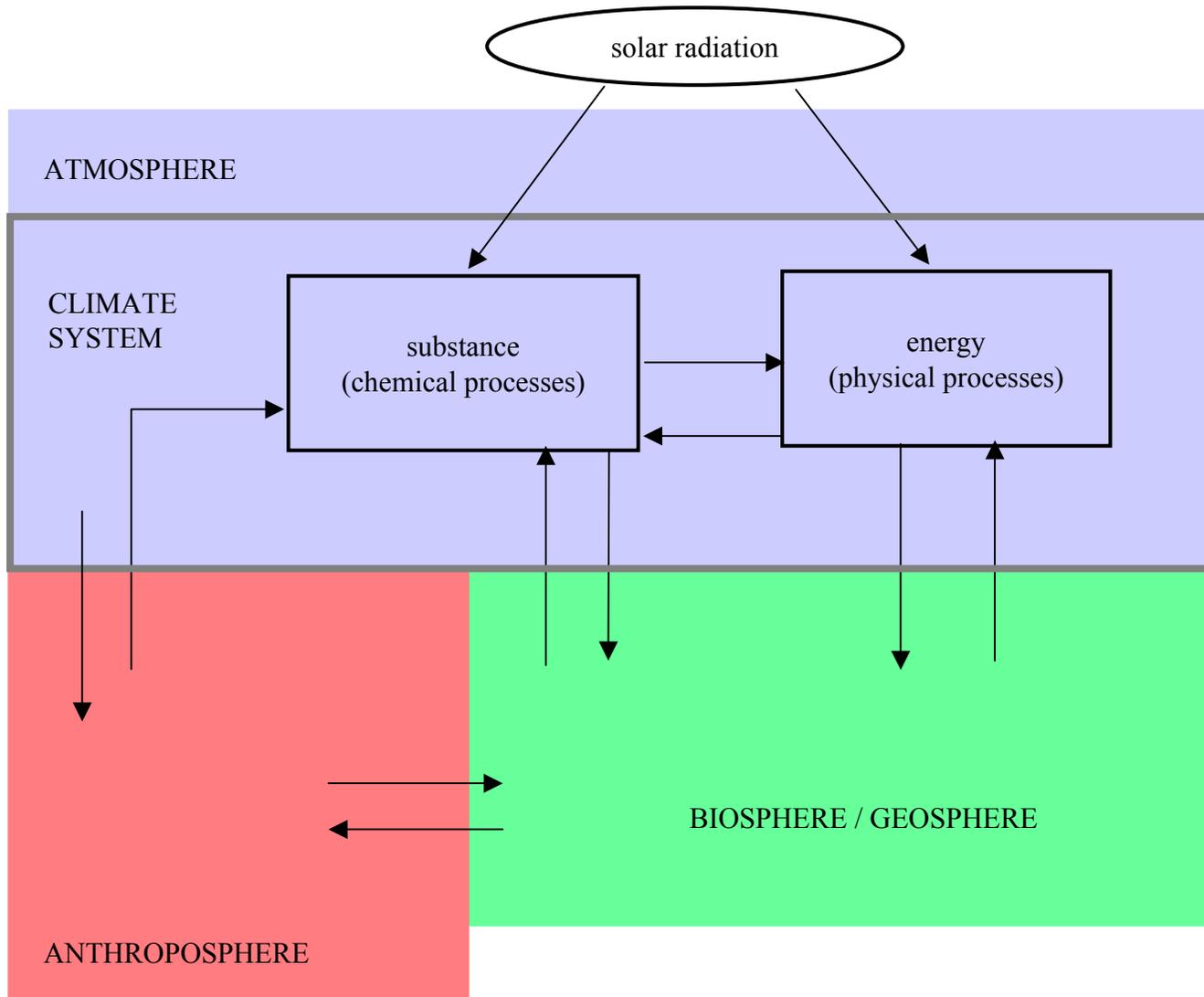
cloud systems, cyclons  
oxidation of SO<sub>2</sub>

interhemispheric transport

oxidation of methane

decay of freons

# The climate system



**clima** [Latin: slope]

**κλίμα** [Greek]

Behind **climate** the meteorologists understand

the sum of meteorological factors (elements) / the summary of weather / the mean (averaged) weather,

describing the **mean status of the atmosphere** at a given site of the Earth surface, represented by the statistical total properties (mean values, frequencies, durations etc.) of a long enough time periode.

(Julius v. Hann 1883, W. Köppen 1923, E. S. Rubinstein 1956, K. Schneider-Carius 1961, J. Blüthgen 1964, WMO 1979)

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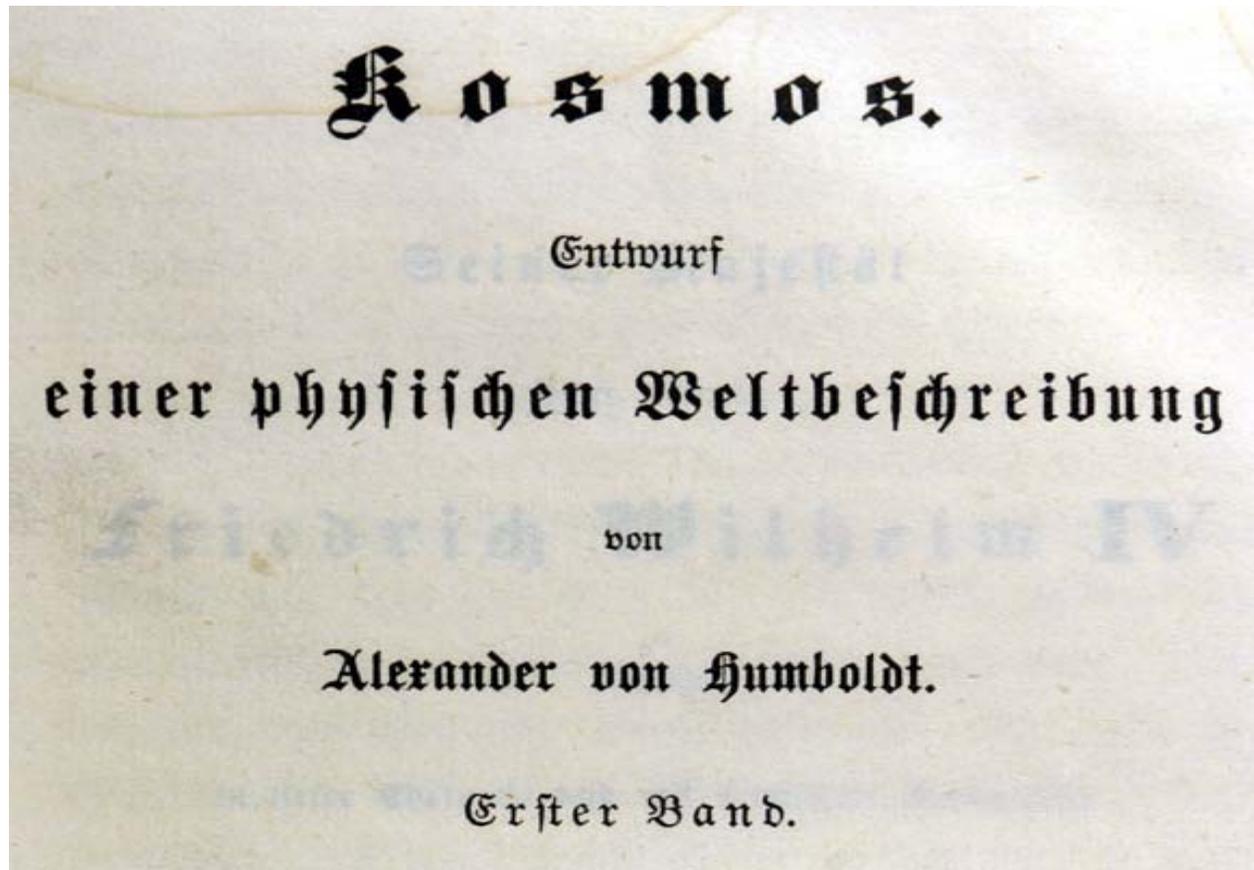
*Climate* is a function of space and time.

*Climate* can not be described as a single unit.

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**Cosmos.**  
Outline  
of a physical world description  
by  
Alexander von Humboldt

First Volume. (1845)



# Climate definition by Humboldt (from: Kosmos, 1845)

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Die Einsicht in die Wärme-Vertheilung im Luftkreise hat einigermaßen an Klarheit gewonnen, seitdem man versucht hat die Punkte, in welchen die mittleren Temperaturen des Jahres, des Sommers und des Winters genau ergründet worden sind, durch Linien mit einander zu verbinden. Das System der Isothermen, Isotheren und Isochimenen, welches ich zuerst im Jahr 1817 aufgestellt, kann vielleicht, wenn es durch vereinte Bemühungen der Physiker allmählig vervollkommnet wird, eine der Hauptgrundlagen der vergleichenden Klimatologie abgeben. Auch die Ergründung des Erd-Magnetismus hat eine wissenschaftliche Form erst dadurch erlangt, daß man die zerstreuten partiellen Resultate in Linien gleicher Abweichung, gleicher Neigung und gleicher Kraft-Intensität mit einander graphisch verband.

Der Ausdruck Klima bezeichnet in seinem allgemeinsten Sinne alle Veränderungen in der Atmosphäre, die unsere Organe merklich afficiren: die Temperatur, die Feuchtigkeit, die Veränderungen des barometrischen Druckes, den ruhigen Luftzustand oder die Wirkungen ungleichnamiger Winde, die Größe der electrischen Spannung, die Reinheit der Atmosphäre oder die Vermengung mit mehr oder minder schädlichen gasförmigen Exhalationen, endlich den Grad habitueller Durchsichtigkeit und Heiterkeit des Himmels: welcher nicht bloß wichtig ist für die vermehrte Wärmestrahlung des Bodens, die organische Entwicklung der Gewächse und die Reifung der Früchte, sondern auch für die Gefühle und ganze Seelenstimmung des Menschen.

Wenn die Oberfläche der Erde aus einer und derselben homogenen flüssigen Masse; oder aus Gesteinschichten zusam-

The term climate denotes in his most general sense all changes in the atmosphere, affecting our organs remarkable: the temperature, the humidity, die barometric pressure change, the silent air status or the impacts of windy airs, the size of electricity, the purity of the atmosphere or its mixing with more or less harmful gaseous exhalations and finally the degree of its transparency and sky-blueness: which not only is important for the increased heat radiation of the soil, the organic development of plants and mature of fruits but also for the human feeling and his spiritual welfare.

# WMO definitions

## Climate

Synthesis of **weather** conditions in a given area, characterized by long-term statistics (mean values, variances, probabilities of extreme values, etc.) of the meteorological elements in that area.

## Weather

The state of the **atmosphere** mainly with respect to its effects upon life and human activities. As distinguished from climate, weather consists of the short-term (minutes to about 15 days) variations of the atmosphere state.

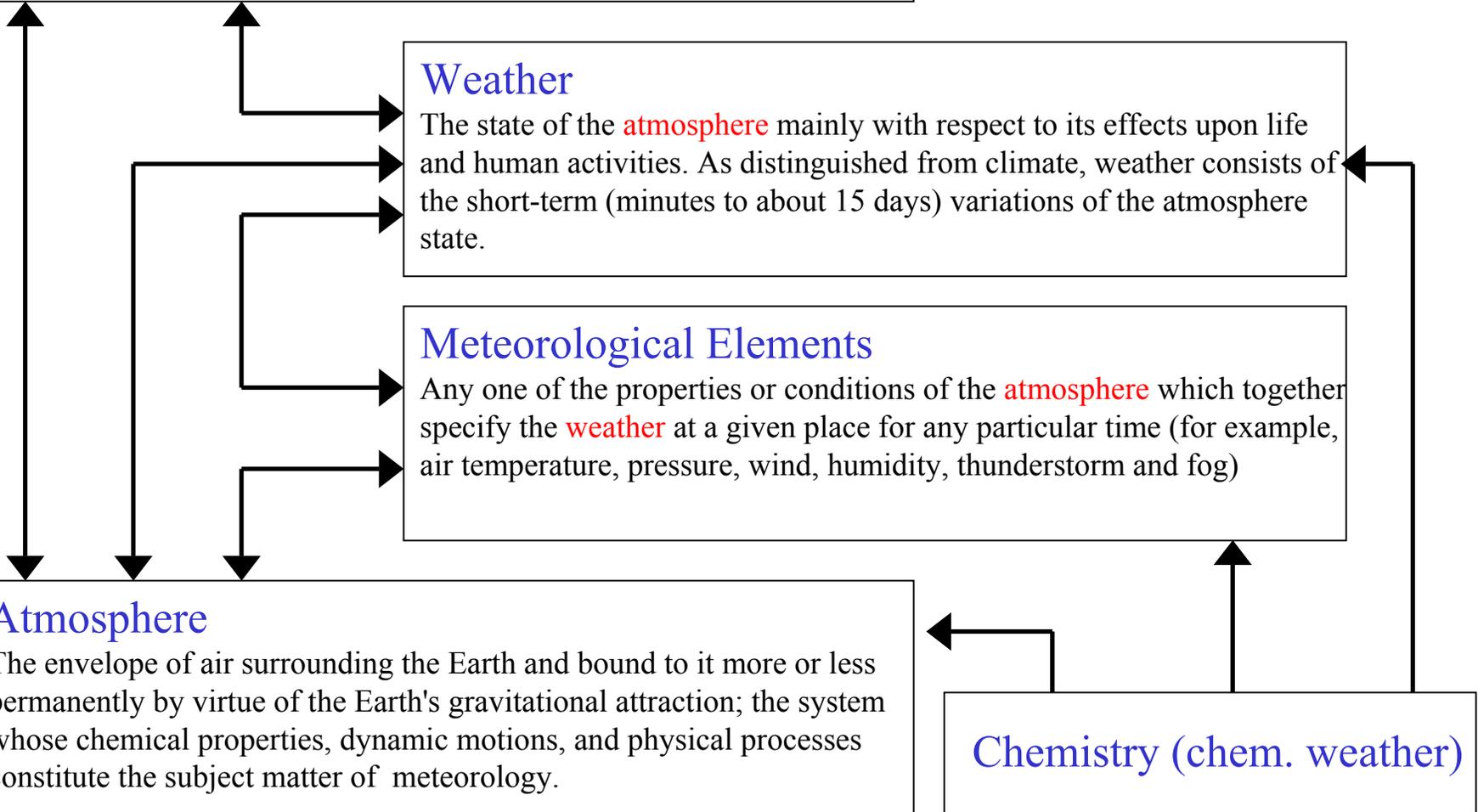
## Meteorological Elements

Any one of the properties or conditions of the **atmosphere** which together specify the **weather** at a given place for any particular time (for example, air temperature, pressure, wind, humidity, thunderstorm and fog)

## Atmosphere

The envelope of air surrounding the Earth and bound to it more or less permanently by virtue of the Earth's gravitational attraction; the system whose chemical properties, dynamic motions, and physical processes constitute the subject matter of meteorology.

## Chemistry (chem. weather)



# Climatological Elements

## *meteorological:*

- temperature
- precipitation
- wind
- cloudiness
- humidity
- sun shine duration
- air pressure
- radiation

## *physico-chemical:*

- deposition (dry, wet)
- trace gas concentration (ozone, greenhouse gase etc.)
- aerosol (number, mass, surface, properties)
- climate forcing
- acidifying potential
- oxidation potential

The term **climate system** often is named by following terms:

- natural Earth system, Ecosphere, Nature (*Alexander von Humboldt*),
- Biosphere (*Vladimir Iwanowitsch Vernadsky*) or
- GAIA (*James Lovelock* and *Lynn Margulis*).

By influencing the natural system by humans it is changing and creating a new „anthropogenic (man-made) system“ (anthroposphere<sup>1</sup>) which, however, is linked with the nature. We can state that new by humans modified Earth system has been developed, the

- Noosphere (*Vladimir Iwanowitsch Vernadskij*)<sup>2</sup>.

Thus, we define among climate system the **Earth System**:

Earth system (= noosphere) = nature + anthroposphere.

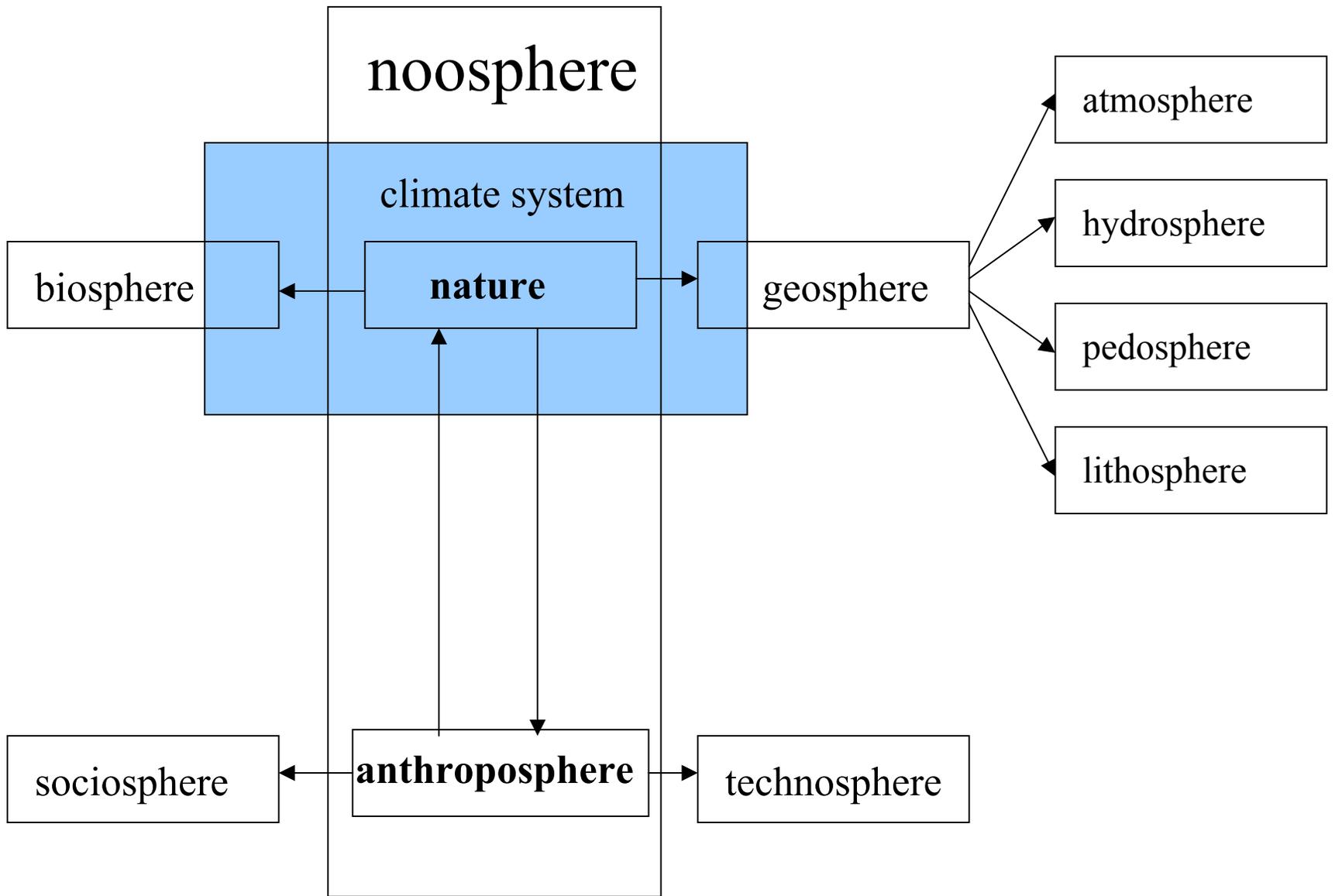
nature = climate system/natural Earth system

anthroposphere = human life sphere (=culture)

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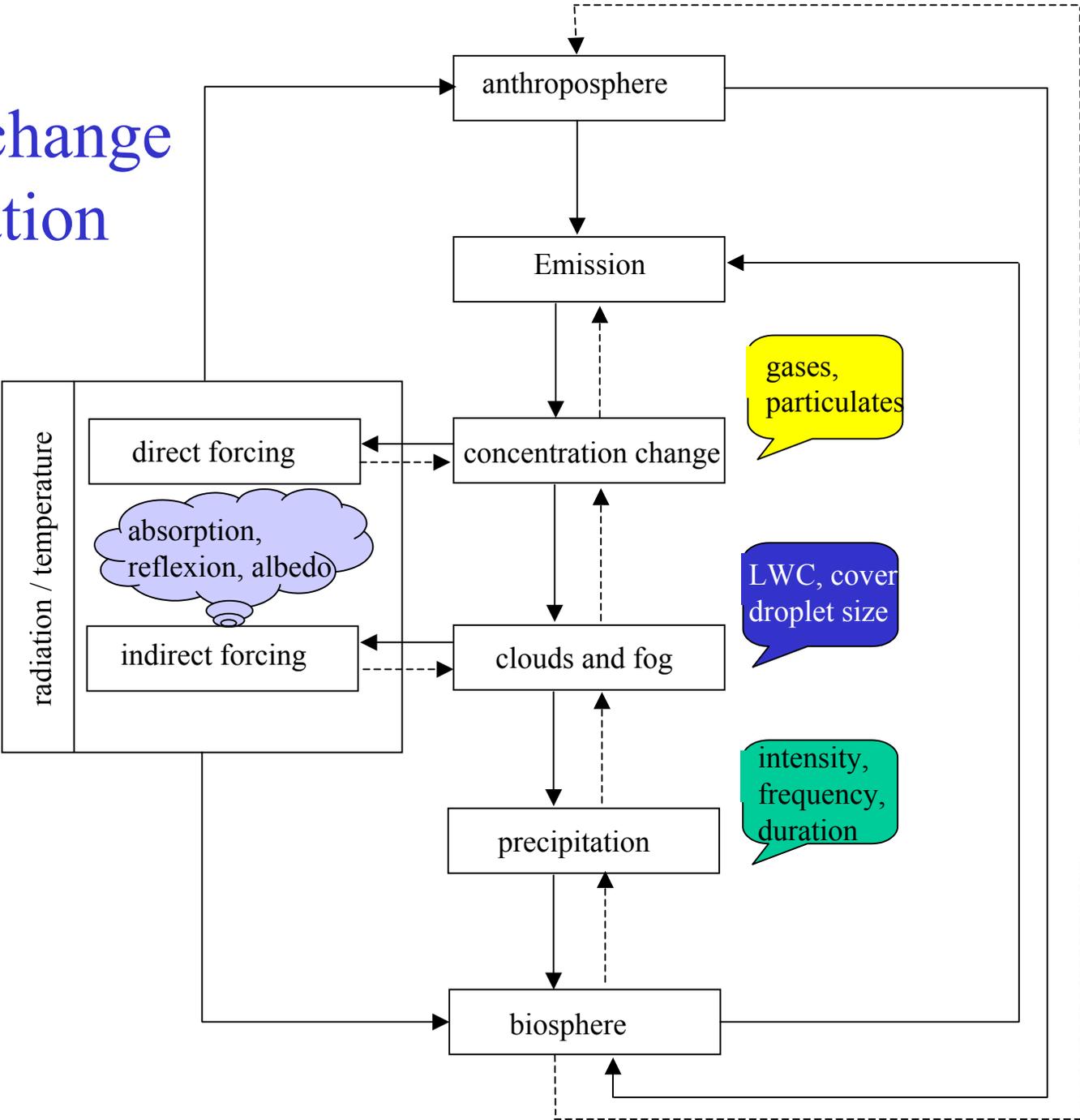
<sup>1</sup> Paul J. Crutzen proposed, to subdivide the present epoch *Holozän* by *Anthropozän*.

<sup>2</sup> This term *Vernadsky* got from the french priest and philosopher *Pierre Teilhard de Chardin* (they met in Paris end of 1920er). V. understood with noosphere a new dimension of the biosphere, developing under the evolutionary influence of humans on natural processes.



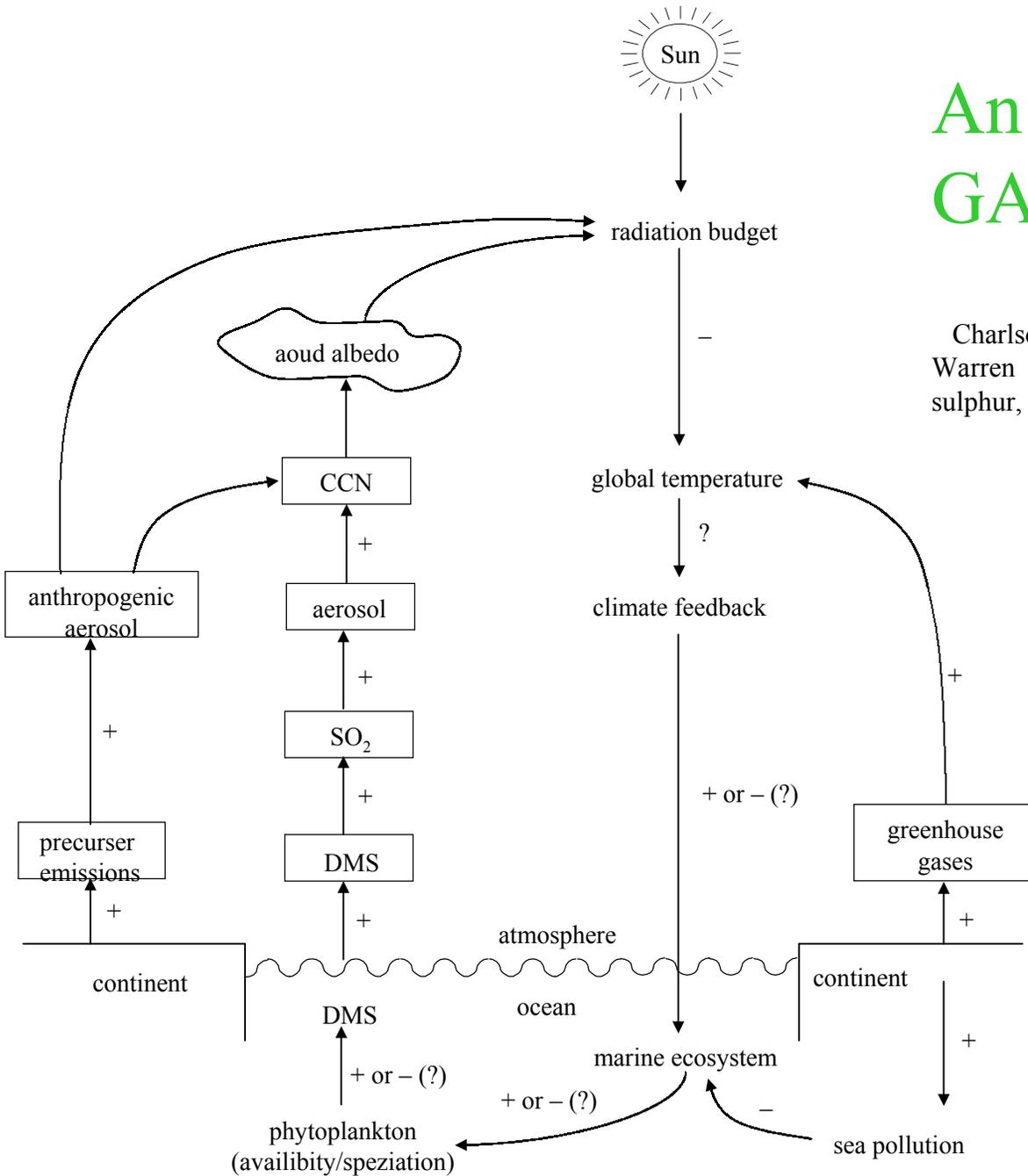
Some examples for complex relationships resulting into **climate change** when system parameters are changing.

# The climate change feedback relation



# An example for the GAIA hypothesis

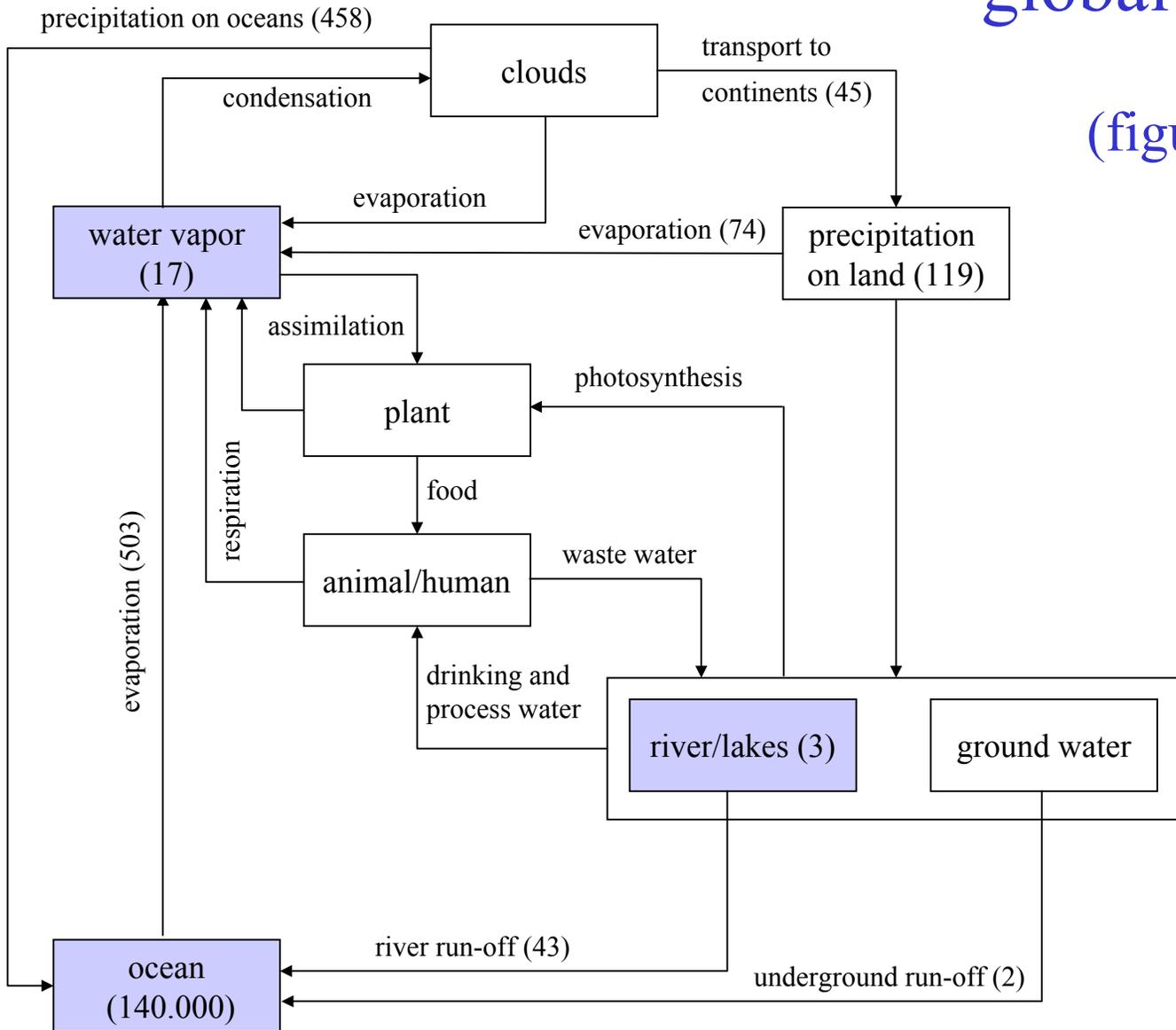
Charlson, R. J., J. E. Lovelock, M. O. Andreae und S. G. Warren (1987) Oceanic phytoplankton, atmospheric sulphur, cloud albedo, and climate. *Nature* **326**, 655-661



# global water cycle

(figures in  $10^3 \text{ km}^3$ )

( $\tau_{\text{H}_2\text{O}} \approx 11 \text{ d}$ )





weather modification:  
1. water resource  
2. mitigate severe weather

