



Soil acidity,
aluminum
toxicity and
nutrient
deficiency

Soil acidity (general info)

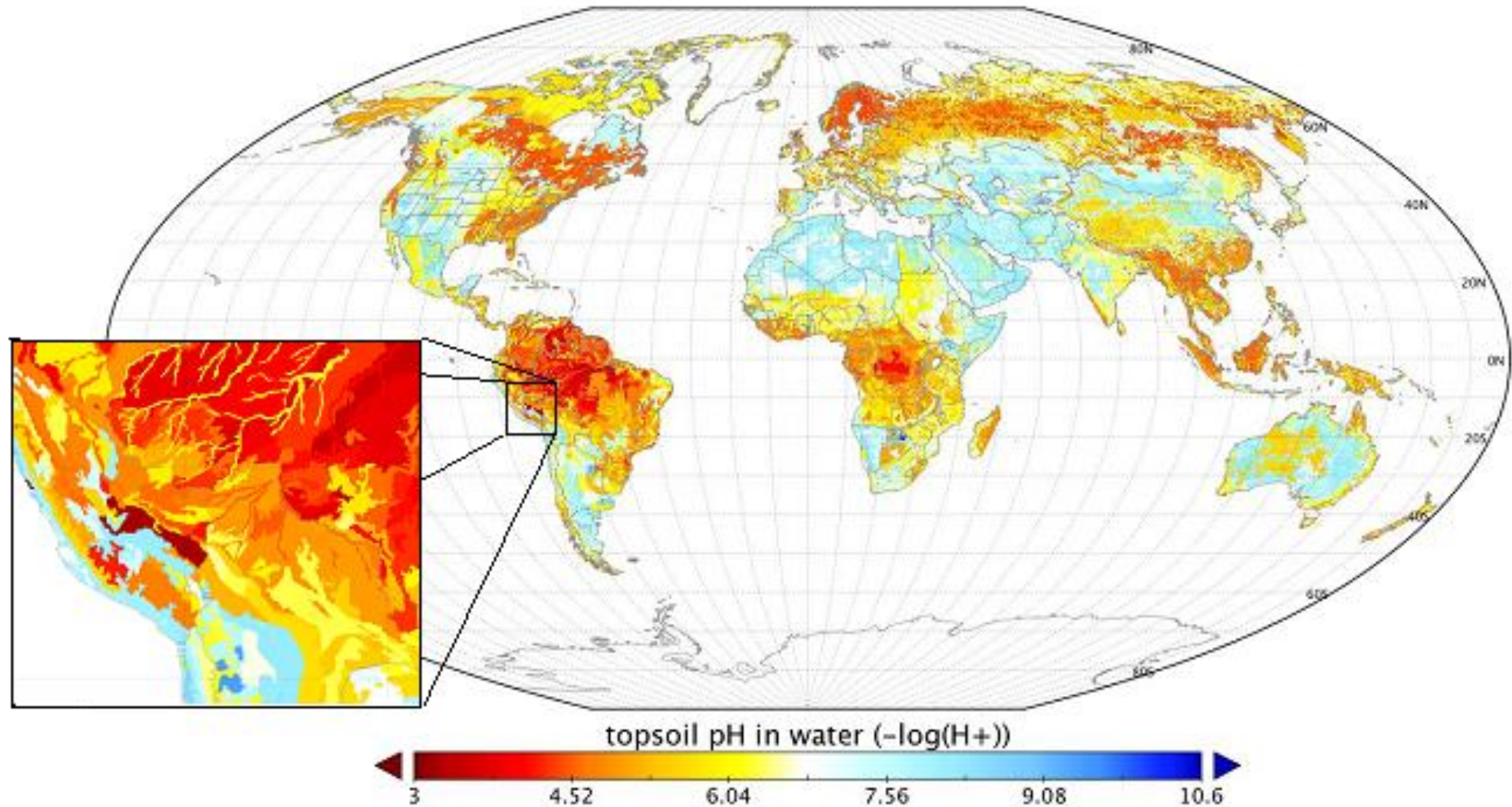
- soil acidification (decrease of soil pH) is negatively affecting the productivity on 30%–40% of the world's agricultural land
- acidification is a natural process (part of soil genesis); in general, decrease of soil pH proceeds in the areas, where precipitation exceeds evapotranspiration (pH drop may be reversed temporarily by liming); human activities have accelerated the rate of acidification and increased the extent of acidic soils
- anthropogenic acidification factors: application of ammoniacal fertilizers, production of N and S oxides due to the combustion of fossil fuels → acid rain; mining activities → weathering of mining waste (sulfides + water + oxygen → sulfuric acid)
- natural acidification factors/processes: biomass decomposition → carboxylic acids; production of gaseous oxides as a result/part of biogeochemical cycles (C, N,...) and their reaction in the atmosphere; emissions of organic compounds from plants (formic acid), atmospheric HCl originates partially from sea-salt aerosols

Important factors

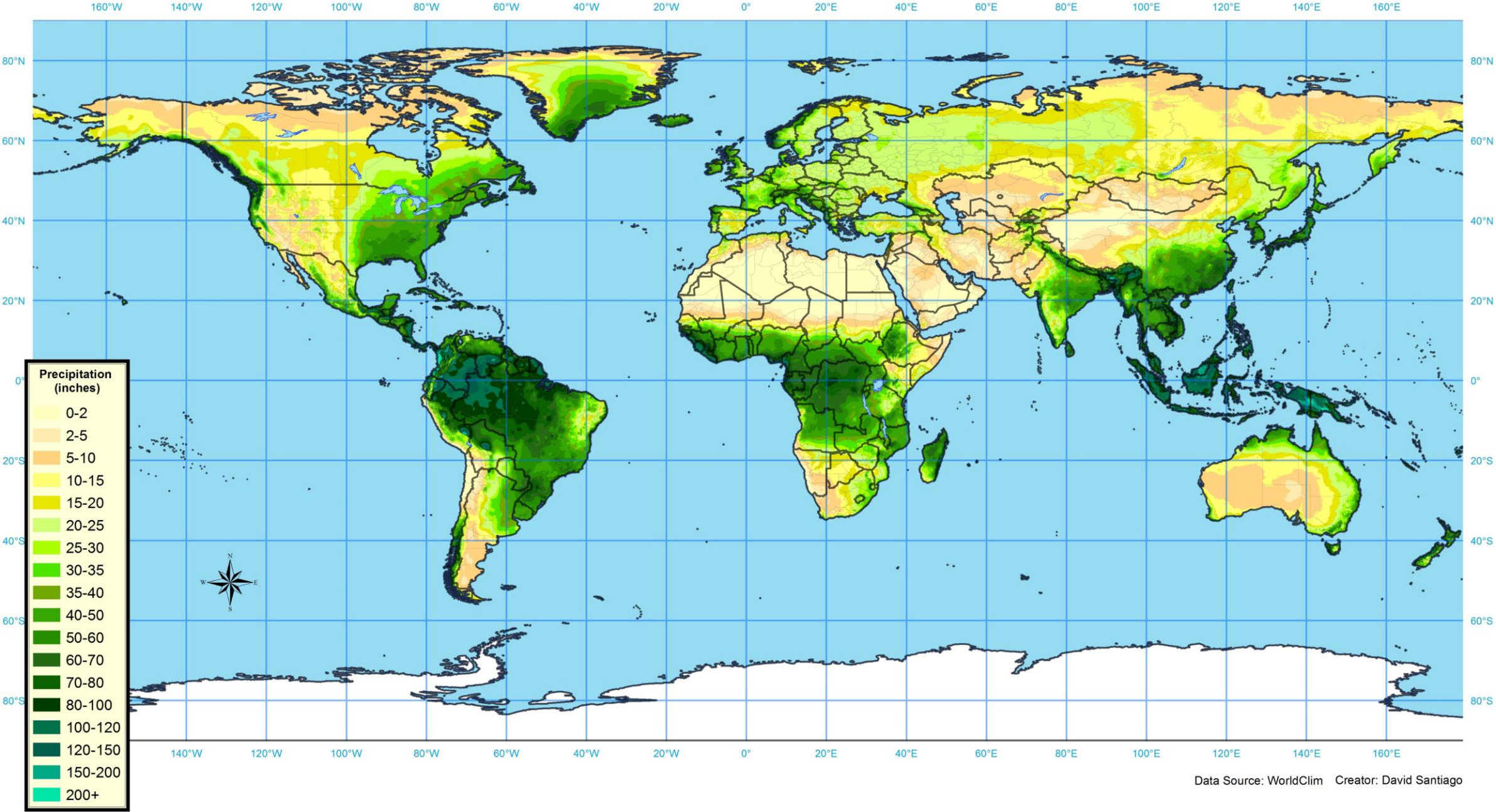
Main aspects / factors that play important role in acidification:

1. precipitation amount (quantitative aspect),
2. chemical composition of precipitation waters (qualitative aspect) !
3. biomass decomposition and liberation of organic acids
4. soil mineralogy and nature of soil parent material !
5. soil water regime

Soil pH in the world → humid and boreal areas show topsoil acidity, whereas soil pH in arid (semiarid) regions is (more or less) alkaline



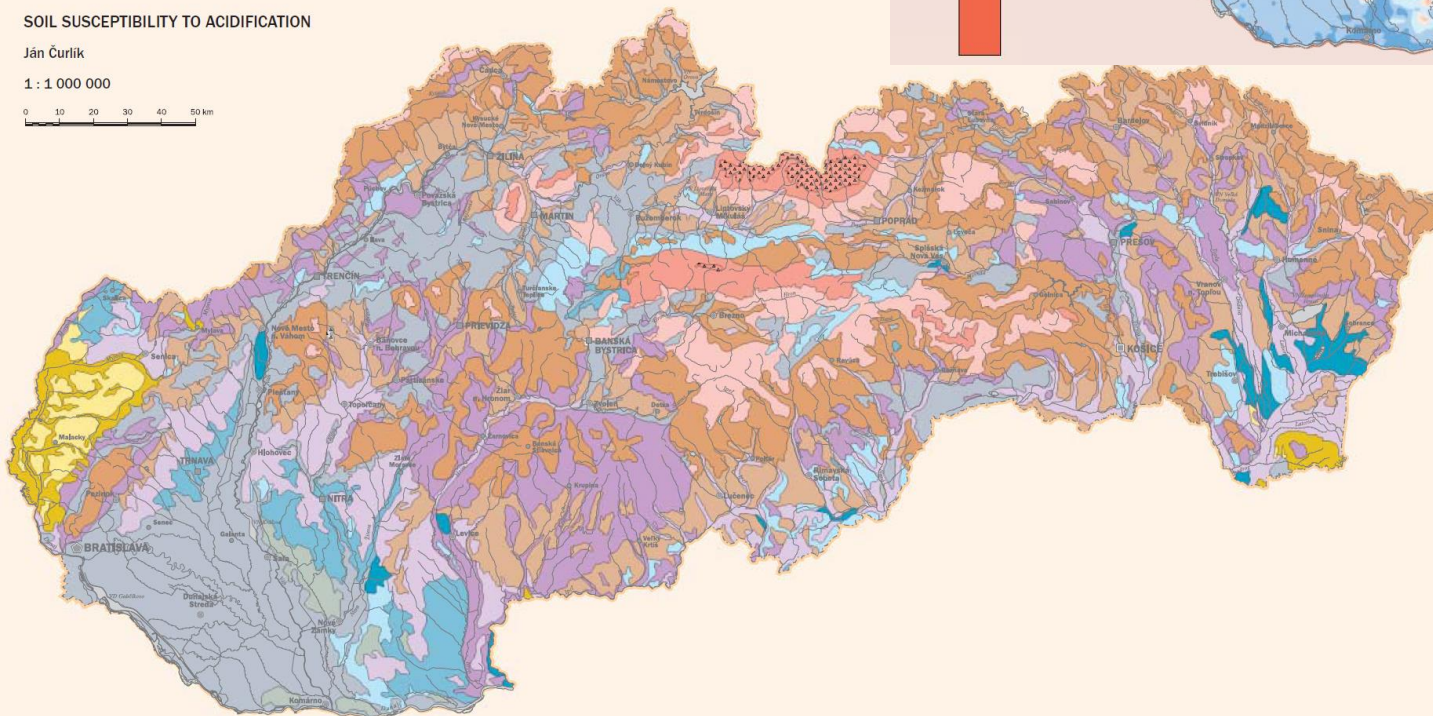
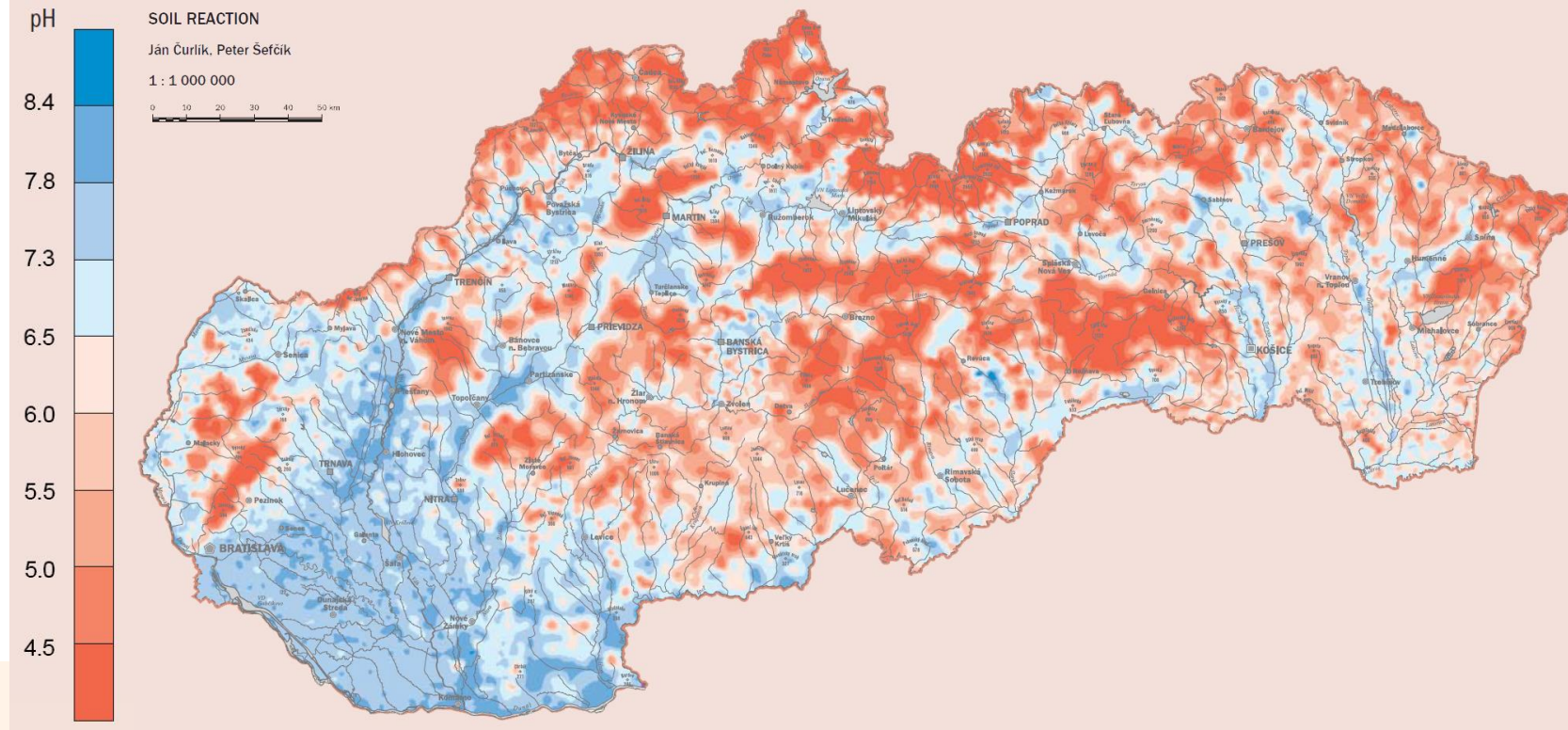
Acidification factors (amount of precipitation)



Soil acidity
(precipitation and character of
soil parent material)

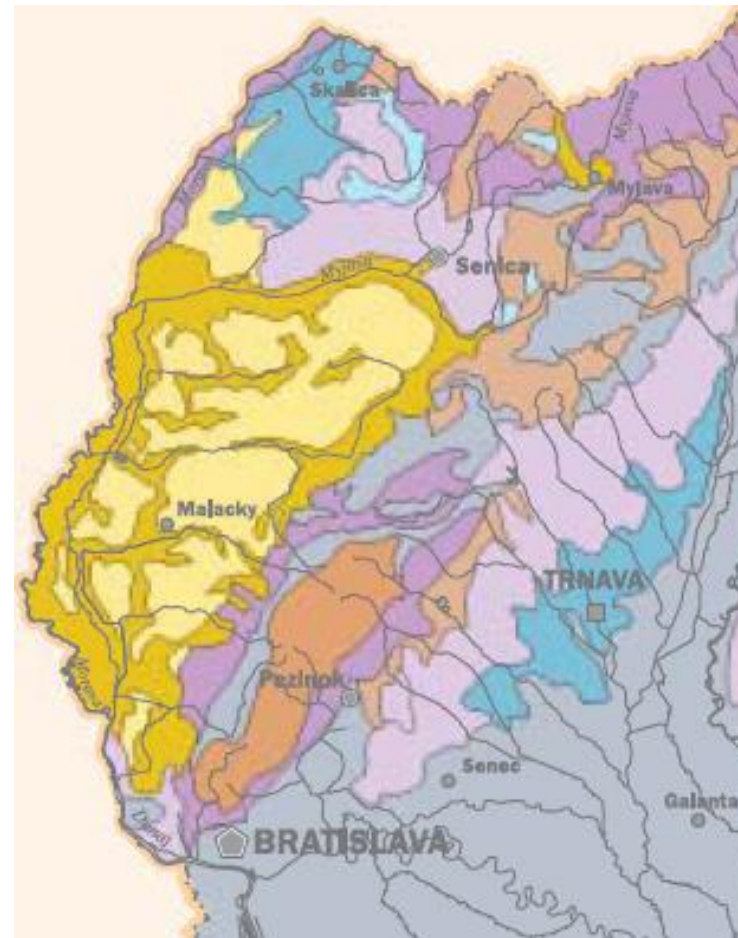
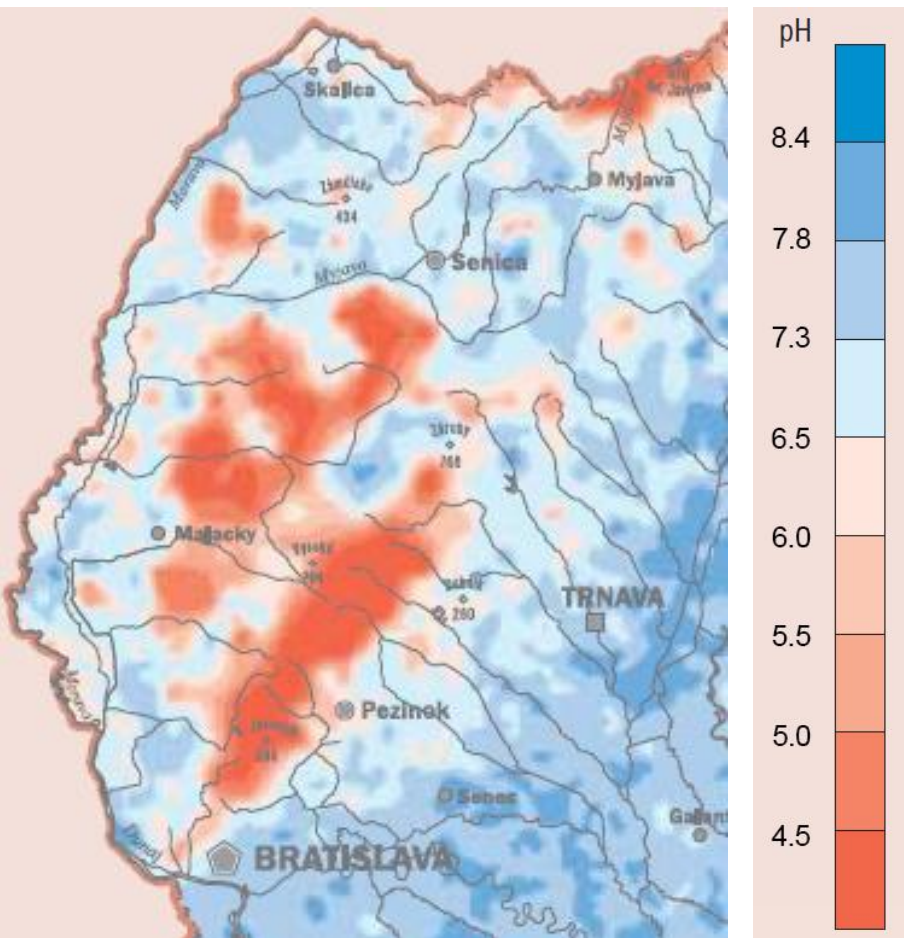
soil pH →

soil susceptibility to acidification



soil susceptibility to acidification ↓

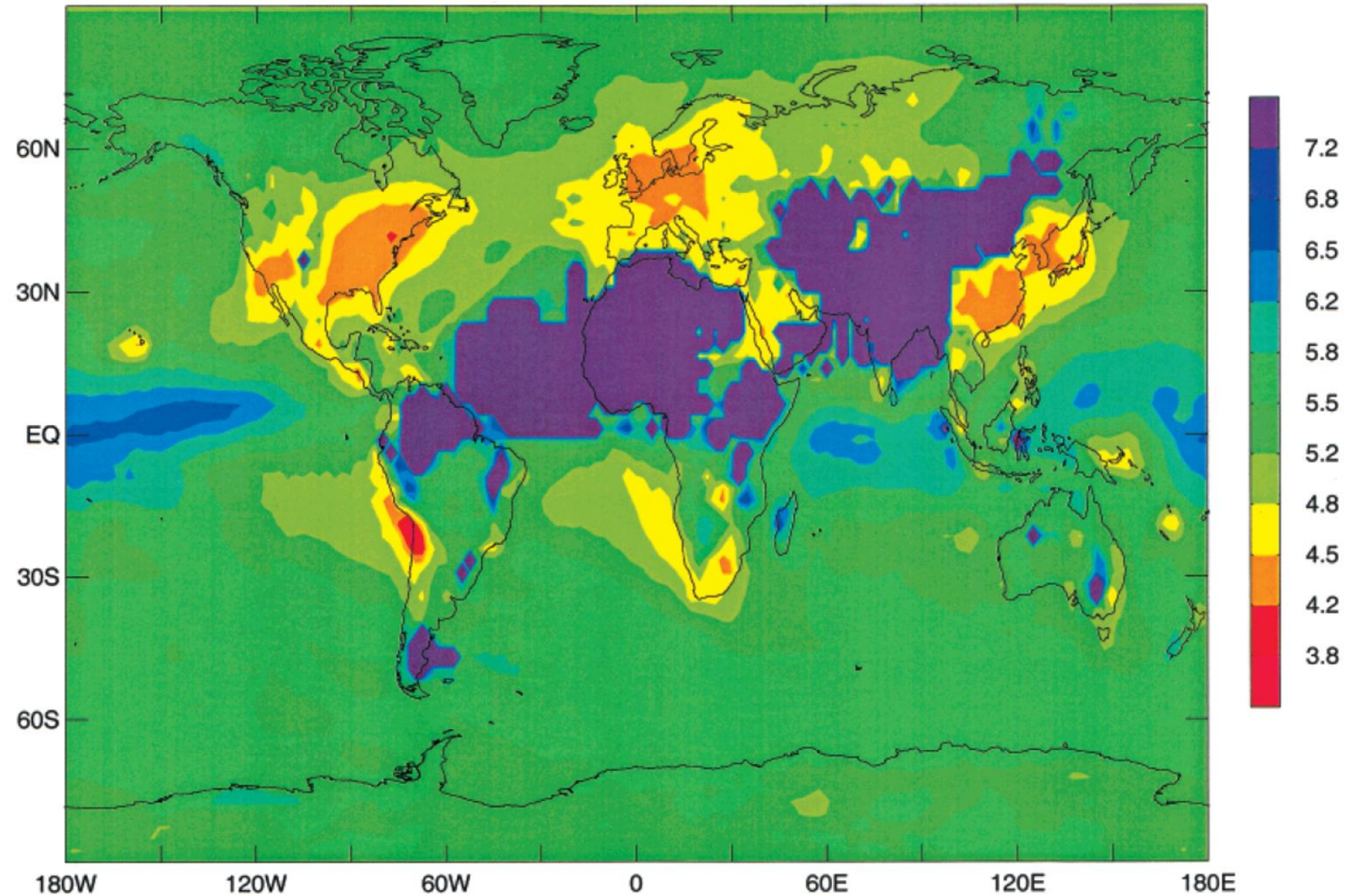
- calcareous soils
- with higher buffer capacity
- with moderate buffer capacity
- with lower buffer capacity
- on the parent rock rich in base cations
- on parent rocks poor in base cations
- humic light textured - to light soils
- low humic light - sandy soils



- altitude or the amount of precipitation are not always important, especially if we compare locations with different soil parent materials
- for example, Záhorie and Danubian Lowland have approximately same altitude and very similar annual precipitation and the pH values are different
- the reason is different soil parent material: soil in the Záhorie are developed from aeolian sands, which are dominantly made of quartz, whereas soil parent material in the Danubian Lowland is made of carbonaceous fluvial deposits

Acidification factors (average pH of rainfall)

Rodhe et al. 2002. The Global Distribution of Acidifying Wet Deposition.



Acidification factors (role of soil parent material)

its composition affects how much protons will be “consumed” by products of weathering reactions

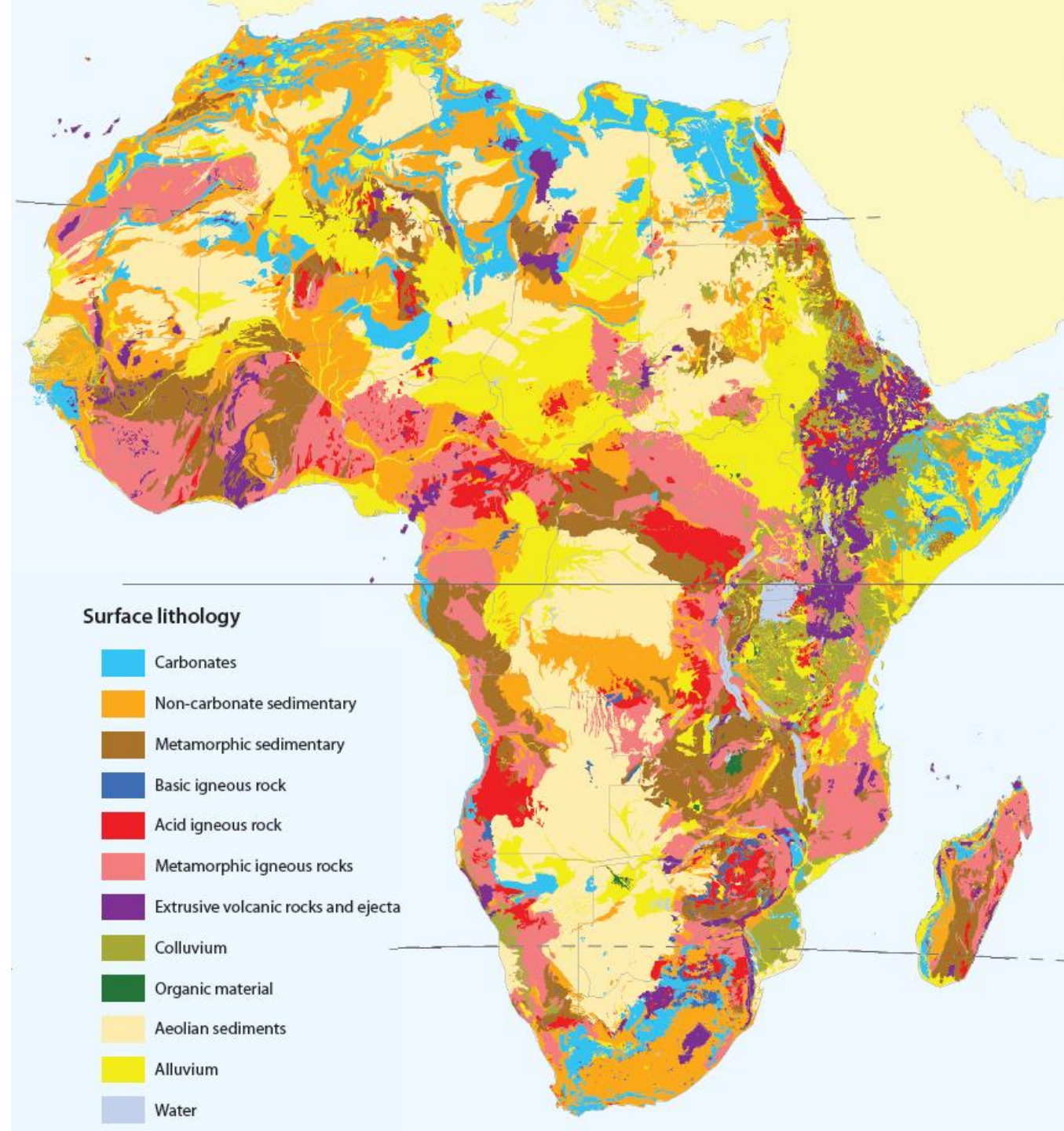
simplified rule: soils with higher portion of SiO_2 in parent material have lower buffering capacity



Acidification factors (role of soil parent material)

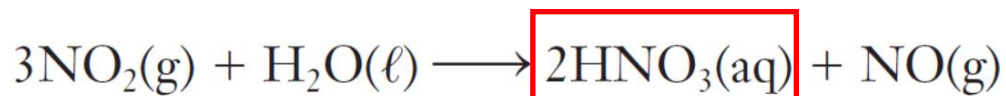
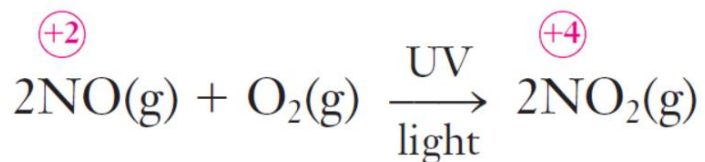
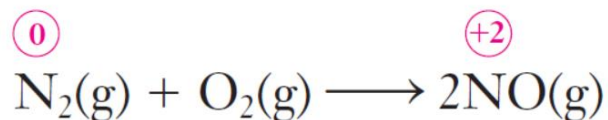
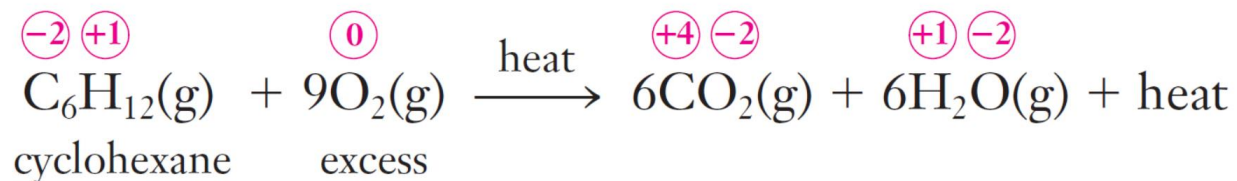
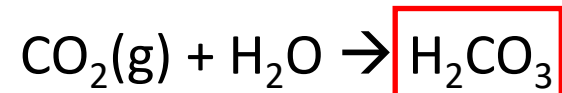
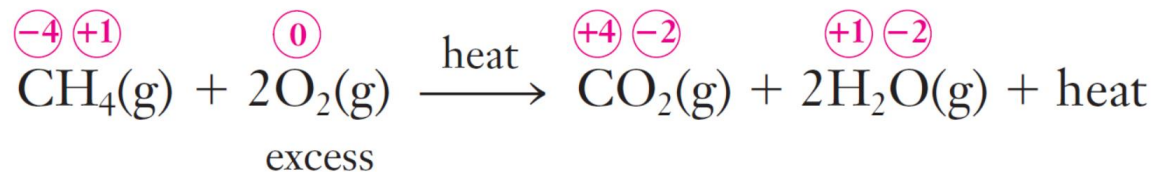
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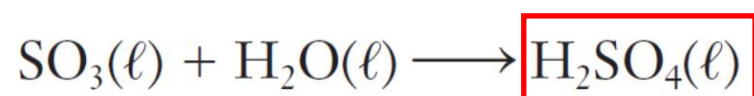
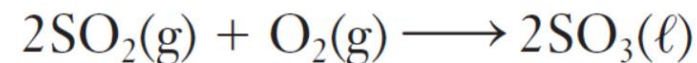
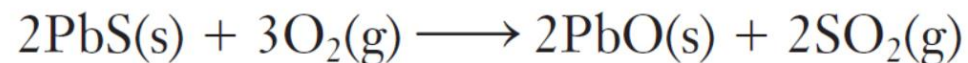
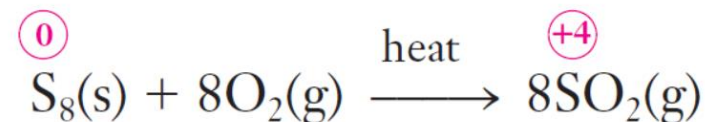


Acidification factors (proton sources)

Origin of protons in the atmosphere: production of gases (oxides) due to the combustion of fossil fuels and other organic materials $\rightarrow$ oxides react with H_2O and $\text{O}_2 \rightarrow$ “acid rain”



coal and oil both
contain up to 5 % of
sulfur; coal also
contains galena
(PbS)



Acidification factors (proton sources from atmosphere)

Origin of protons in the atmosphere: production of gases (oxides) due to the combustion of fossil fuels and organic materials $\rightarrow$ oxides react with H_2O and $\text{O}_2 \rightarrow$ “acid rain”

- burning of organic matter (fossils) $\rightarrow \text{CO}_2 \rightarrow \text{H}_2\text{CO}_3$
- coal often contains sulfur, combustion $\rightarrow \text{SO}_2 \rightarrow \text{SO}_3 \rightarrow \text{H}_2\text{SO}_4$
- making of pulp and/or paper from wood and other cellulosic materials $\rightarrow \text{HCl}$
various plastics and synthetic organic compounds contain Cl, combustion $\rightarrow \text{HCl}$
- NO generated from the air that is mixed with the fuel during combustion in engines;
NO reacts with O_2 in the atmosphere to $\rightarrow \text{NO}_2$, which further react with water to form HNO_3

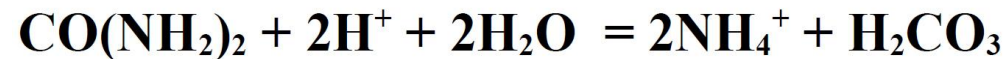
Acidification factors (proton sources)

Some (nitrogen) fertilizers are acidic

Modern fertilizers commonly use ammonium (NH_4^+) as the nitrogen source, but the eventual conversion of ammonium to nitrate (NO_3^-) is accompanied by release of hydrogen protons



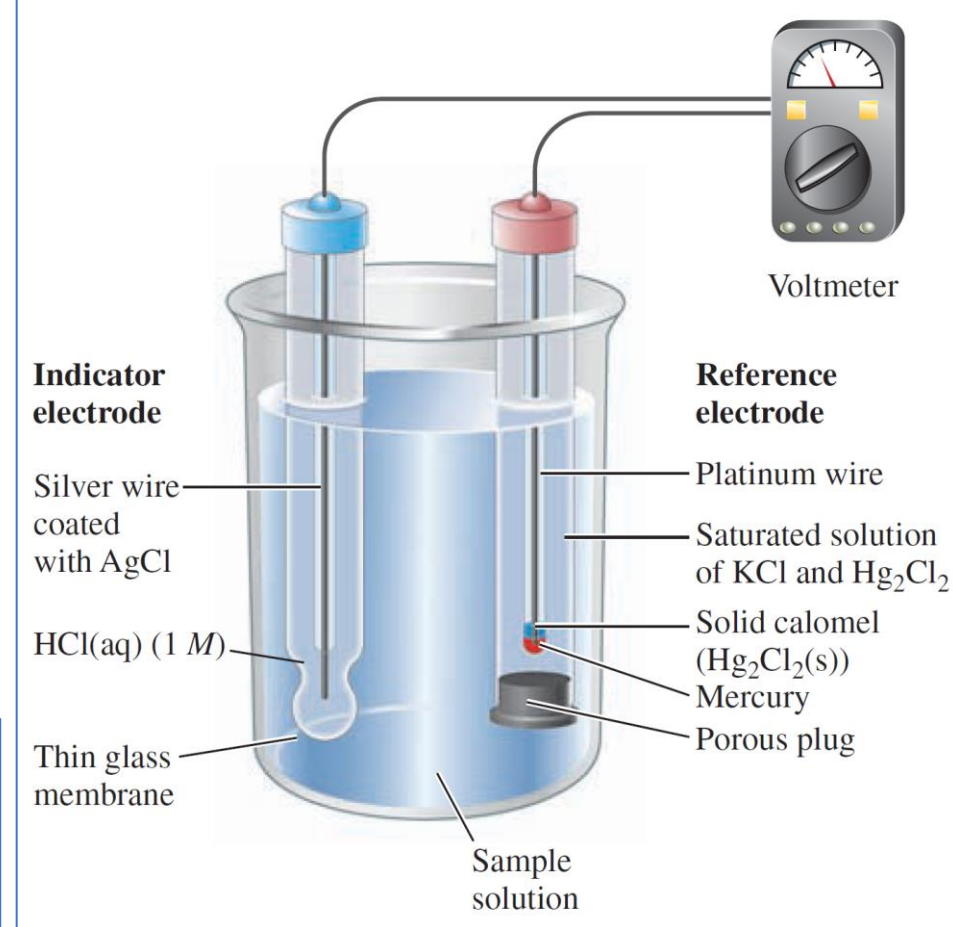
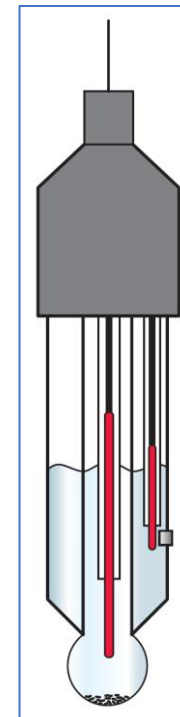
A popular nitrogen fertilizer is urea, which in soil (with pH less than 6.3) is decomposed as follows:



Soil pH

- important soil property and indicator of soil quality
- parameter obtained by potentiometry using glass electrode
- based on the pH value we can predict (approximately): availability of soil nutrients, activity of microorganisms (fungi vs. bacteria), mobility and toxicity of elements, quality of soil organic matter
- it is a parameter of solution (soil is a more complex system than solution; three phases: solid, liquid, gas)
- pH of most soils ranges between 3 and 9

modern – combined pH electrodes →



pH (origin)

- even pure water has slight (very low) electric conductivity (0.055 $\mu\text{S}/\text{cm}$), why? because of ions (H_3O^+ , OH^-); autoprotolysis of water: small portion of H_2O molecules dissociates (Svante Arrhenius, Sweden)
- the concept $\text{pH} = -\log [\text{H}_3\text{O}^+]$ was introduced by Danish chemist Søren Sørensen in 1909
- for equation $2\text{H}_2\text{O} = \text{H}_3\text{O}^+ + \text{OH}^-$ we can write an equilibrium constant (K_a):

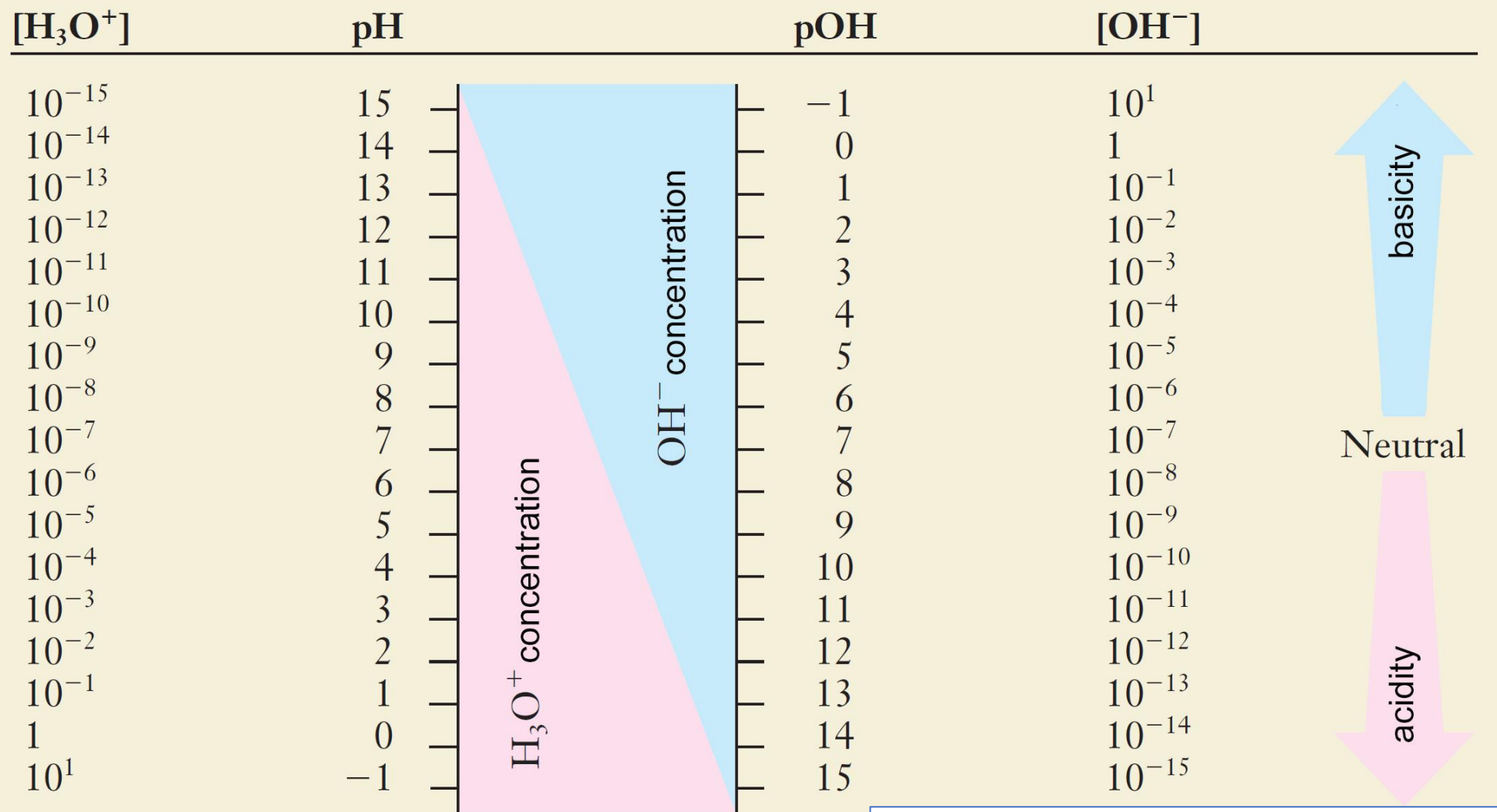
$$K_a = \frac{a_{\text{H}_3\text{O}^+} a_{\text{OH}^-}}{a_{\text{H}_2\text{O}}^2}$$

equilibrium of the reactions will be shifted towards the left, which means that we can plug 1 for $a_{\text{H}_2\text{O}}$

$$\underset{\downarrow 10^{-14}}{K_w} = a_{\text{H}_3\text{O}^+} a_{\text{OH}^-} = \underset{\downarrow 10^{-7}}{c_{\text{H}_3\text{O}^+}} \underset{\downarrow 10^{-7}}{c_{\text{OH}^-}} f_{\text{H}_3\text{O}^+} f_{\text{OH}^-}$$

since we are dealing with very dilute solution, we can replace activity coefficients with ≈ 1

We know that water dissociation constant (ionic product of water) $K_w = 1 \times 10^{-14}$ and $\text{pH} = -\log [\text{H}_3\text{O}^+]$
if concentration of both, H_3O^+ and OH^- will be equal $= 10^{-7} \rightarrow \text{pH} = 7 \rightarrow$ therefore pH often ranges from 0 to 14, but it may exceed this range if the concentration of H_3O^+ or OH^- will be $> 1 \text{ mol L}^{-1}$
pH changes logarithmically $\rightarrow$ it means that one unit drop, or increase, is caused by 10 x change in concentration



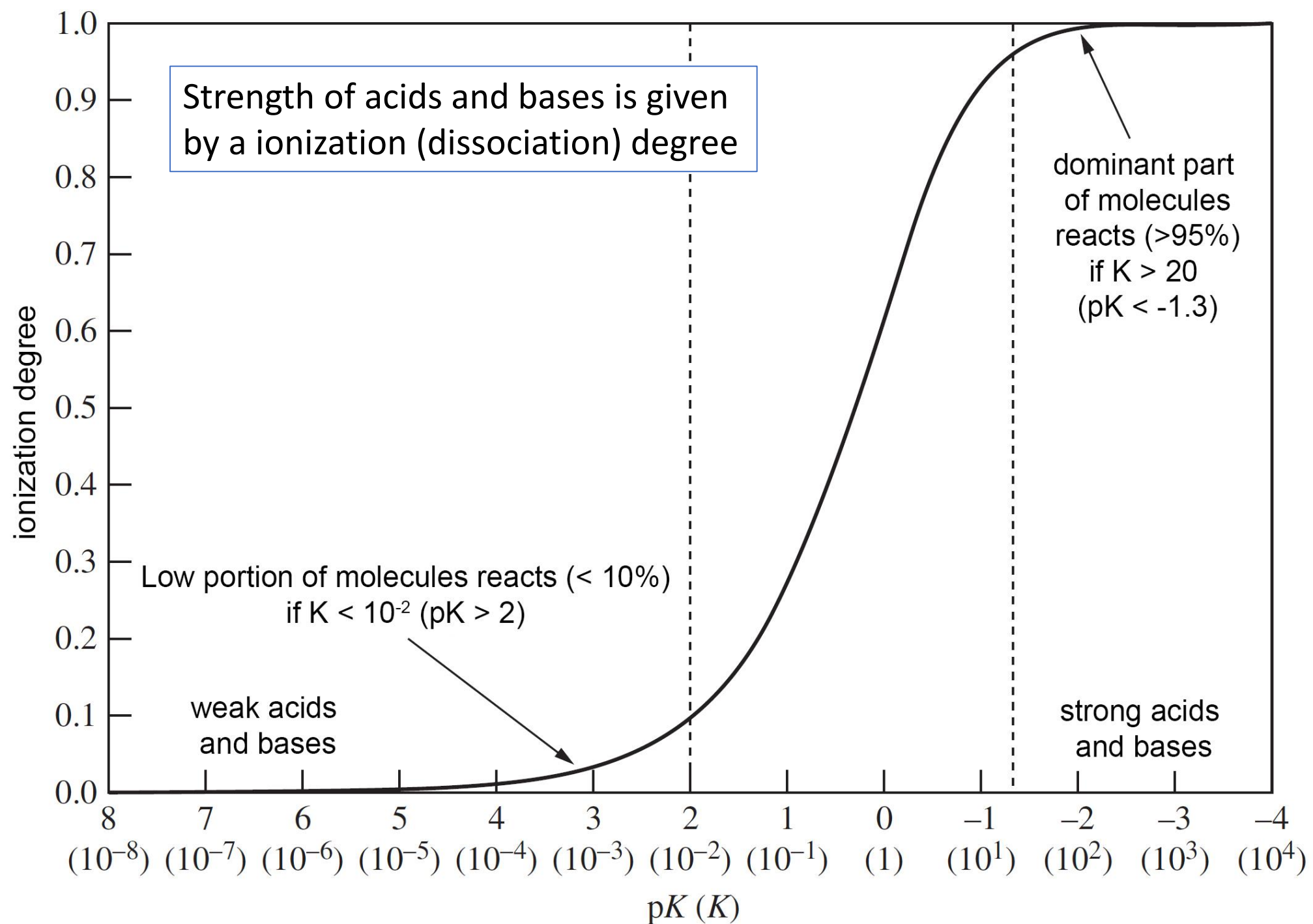
$\text{pH} = 3.53 \rightarrow [\text{H}_3\text{O}^+] = 10^{-3.53} = 2.95 \times 10^{-4} \text{ mol l}^{-1}$
 $\text{pOH} = 11.40 \rightarrow [\text{OH}^-] = 10^{-11.40} = 3.98 \times 10^{-12} \text{ mol l}^{-1}$
 $[\text{H}_3\text{O}^+] = 1.2 \text{ mol l}^{-1} \rightarrow \text{pH} = -\log 1.2 = -0.08$
 $[\text{OH}^-] = 0.09 \text{ mol l}^{-1} \rightarrow \text{pOH} = -\log 0.09 = 1.05$

Strength of the acids

- the strength (ability to dissociate / donate protons) of an acid is defined by the equilibrium (acidity) constant (K_a), called also dissociation constant
- similarly to pH, there is pK index, which is a negative logarithm of K_a
- as pK value decreases, the strength of an acid increases (portion of dissociated molecules increases)
- for a carboxylic acid we can write:

$$K_a = \frac{(RCOO^-)(H^+)}{RCOOH}$$

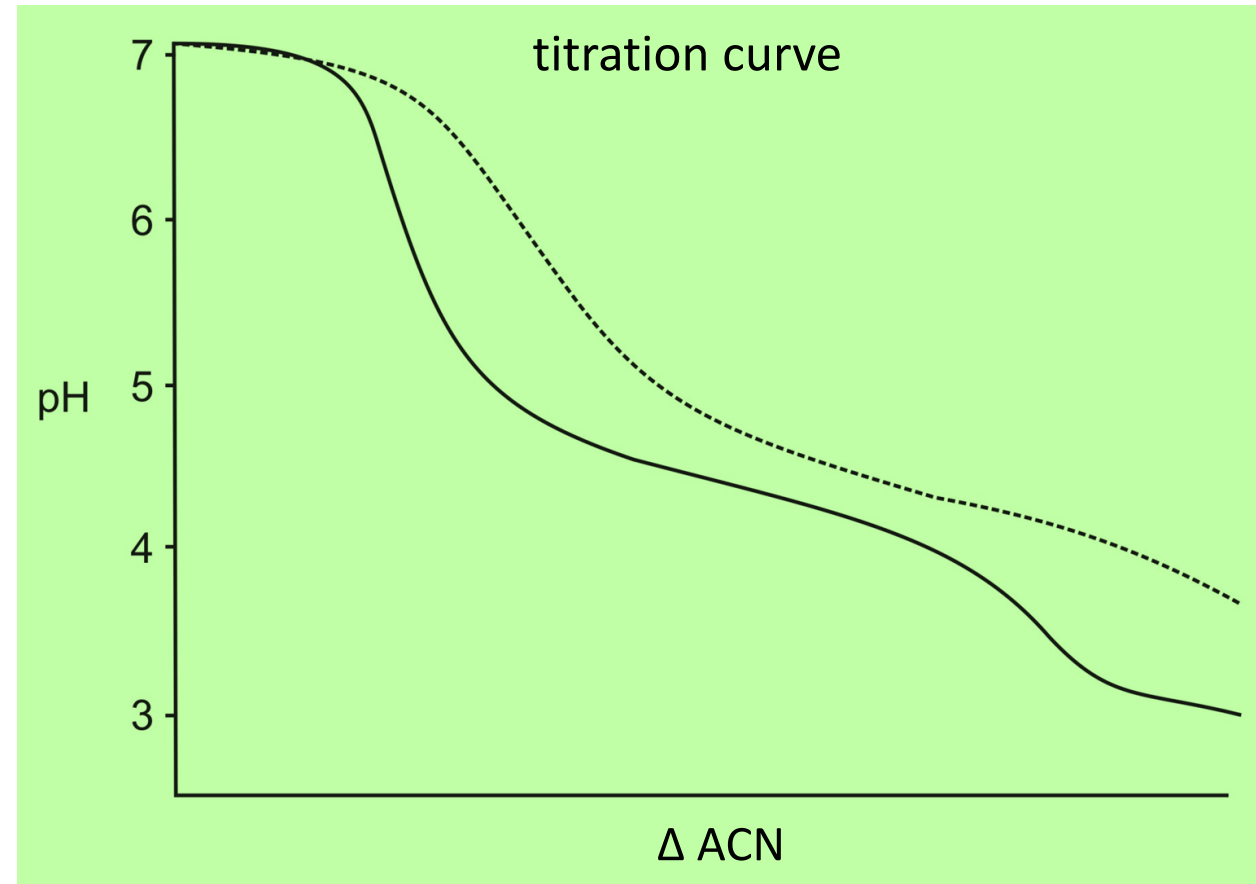
- some acids have more than one proton, for example, $H_2SO_4 \rightarrow$ the pK of first dissociation will be lower (-2.8) compared to second (1.99)
- pK of most soil carboxylic acids ranges from 3 to 6
 $Al^{3+} + H_2O = AlOH^{2+} + H^+$ (pK = 5)
 $H_2CO_3 = HCO_3^- + H^+$ (pK = 6.35)
- besides strength of given acid and specific chemical reaction, the **amount and concentration of protons** is important (considering in situ soil conditions). For example, H_2SO_4 is stronger acid in comparison to H_2CO_3 , but its concentration in precipitation water is usually lower; moreover, we often don't know the origin of the protons (H_2SO_4 , H_2CO_3 ,...), when we measure pH



Acid neutralization capacity of soils (two components are recognized: solid and liquid)

- solid phase – ANC_S
 ANC_S (for a soil with pH 5) $\approx 2[CaO] + 2[MgO] + 2[K_2O] + 2[NaO] + 2[FeO] + [NH_3] - 2[SO_3] - 2[P_2O_5] - [HCl] - 2[N_2O_5]$
- liquid phase – ANC_L
 ANC_L (for a soil with pH 5) $\approx [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] + [A^-] - [H^+]$

from practical viewpoint acid neutralization capacity of solid phase is much more important, because dissolved species in soil solution are rapidly consumed

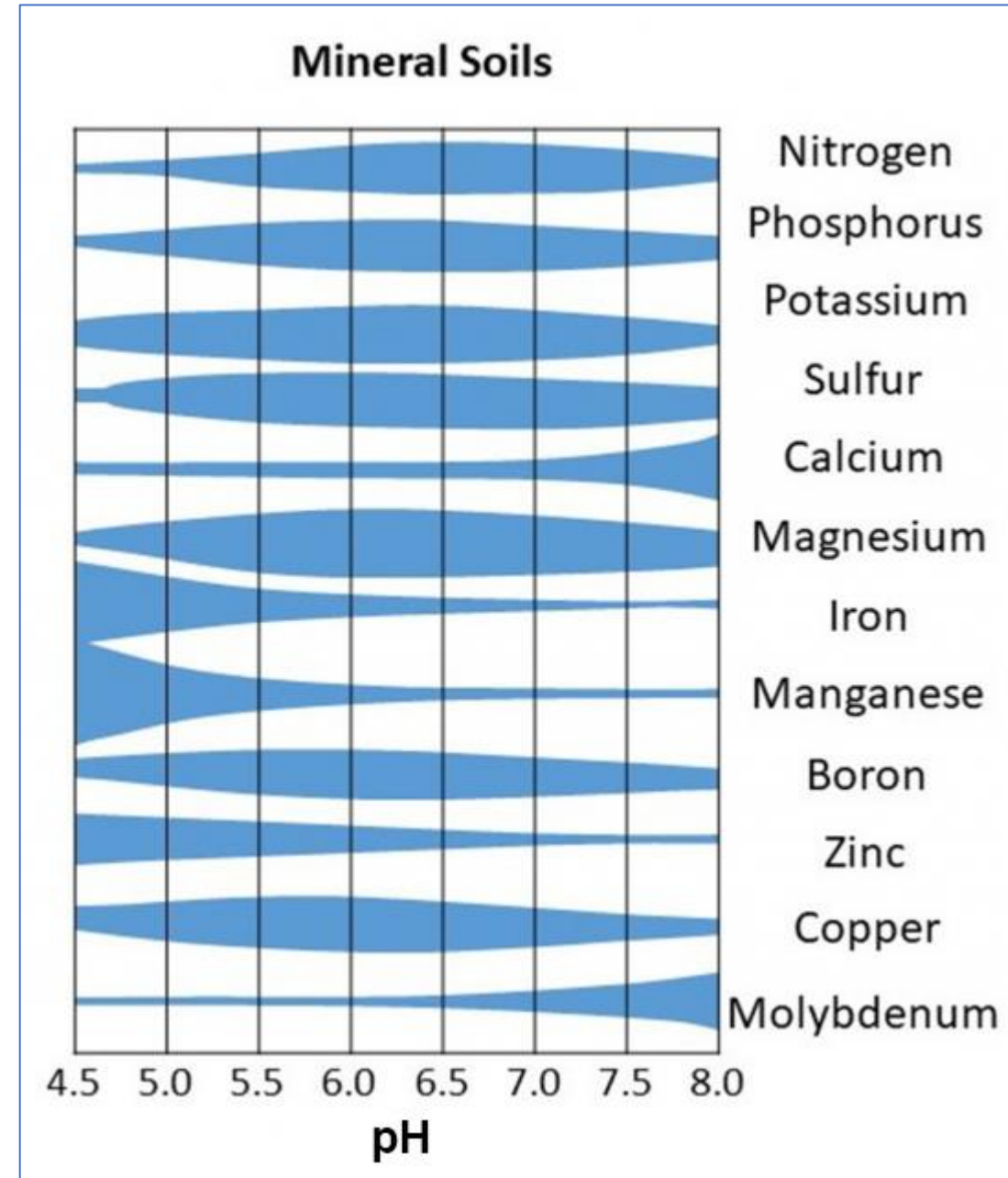
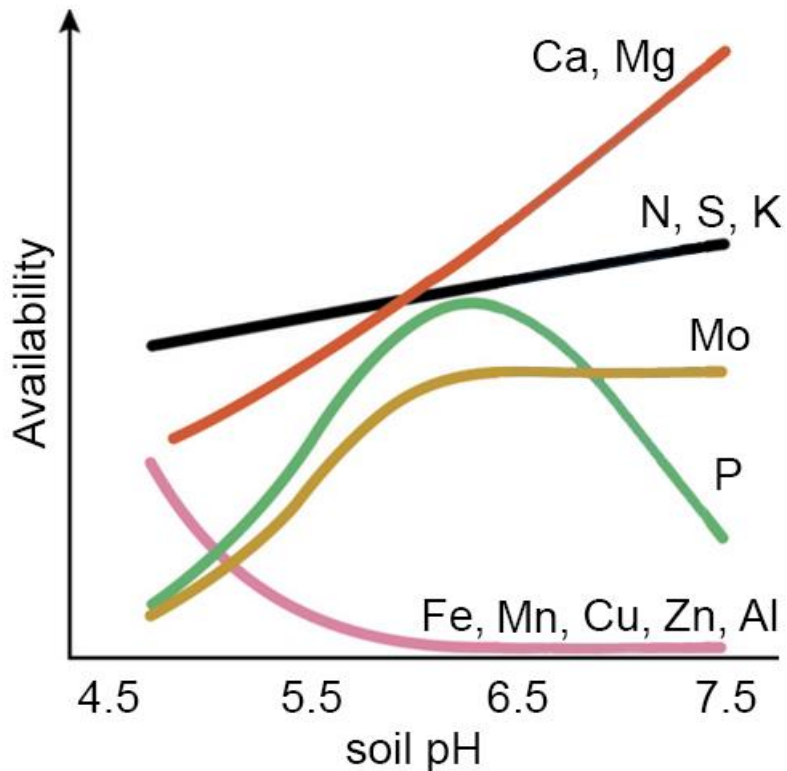


Soil acidity buffering

Buffer Substance	pH range	Reactions
Limestone, CaCO_3	7 - 9.5	Dissolution and precipitation
Oxides and hydroxides of Fe and Al; silicate clay edges	whole pH range	H^+ adsorption and desorption on surface hydroxyl sites
H^+ –soil organic matter	whole pH range	Dissociation and protonation of carboxyl and phenol groups
Al –soil organic matter and $\text{Al}(\text{OH})_3$ (s)	5 - 8	Precipitation of organic bound Al^{3+} as $\text{Al}(\text{OH})_3$ or dissolution of $\text{Al}(\text{OH})_3$ by organic acids
$\text{Al}^{3+}/\text{H}^+$ exchange in soil organic matter	< 4.5	H^+ exchange with Al^{3+} on carboxyl and phenol groups
$\text{Al}(\text{OH})_3$	4 - 5.5	$\text{Al}(\text{OH})_3$ dissolution/precipitation in soils with very low organic matter content
Silicate clay interlayer $\text{Al}(\text{OH})_n^{3-n}$ in 2:1 clays	4.2 - 7	Hydrolysis and precipitation or dissolution of interlayer $\text{Al}(\text{OH})_3$
Permanent charge silicate clays	3.5 - 4.2	Ion exchange of H^+ and Al^{3+}
Irreversible dissolution of high-activity 2:1 silicate clays and poorly ordered aluminosilicates	< 3.5	Consumes H^+ upon release of Al^{3+} from reactive silicates
Very slow irreversible weathering primary silicate minerals	whole pH range	Consumes H^+ upon dissolution of Ca^{2+} , Mg^{2+} , K^+ , and Na^+ from primary minerals

Soil pH and nutrient availability / mobility

- if soil pH < 5.5 → lower availability of P, it forms insoluble compounds with Fe
- if soil pH < 4.2 other soil nutrients are either missing (due to leaching) or not accessible (insoluble, strongly adsorbed)



Negative consequences of soil acidity (aluminum toxicity)

- Al is the third most abundant element in Earth's crust (after O and Si); various primary (mica, feldspar, pyroxene, amphiboles) and secondary minerals (clays, oxyhydroxides) contain Al
- lower Al content is characteristic for carbonates or sandstones
- weathering → release of Al into soil solution (different chemical forms)
- if soil pH < 4 → formation of hydrated Al species → toxic effects on plant roots
- toxicity: limited growth and degeneration of root system, limited uptake of nutrients (P, Ca, Mg, N); in acidic soils the toxicity of Fe and Mn takes place as well
- in acid environment $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ (toxic form) is stable, in literature denoted often simply as

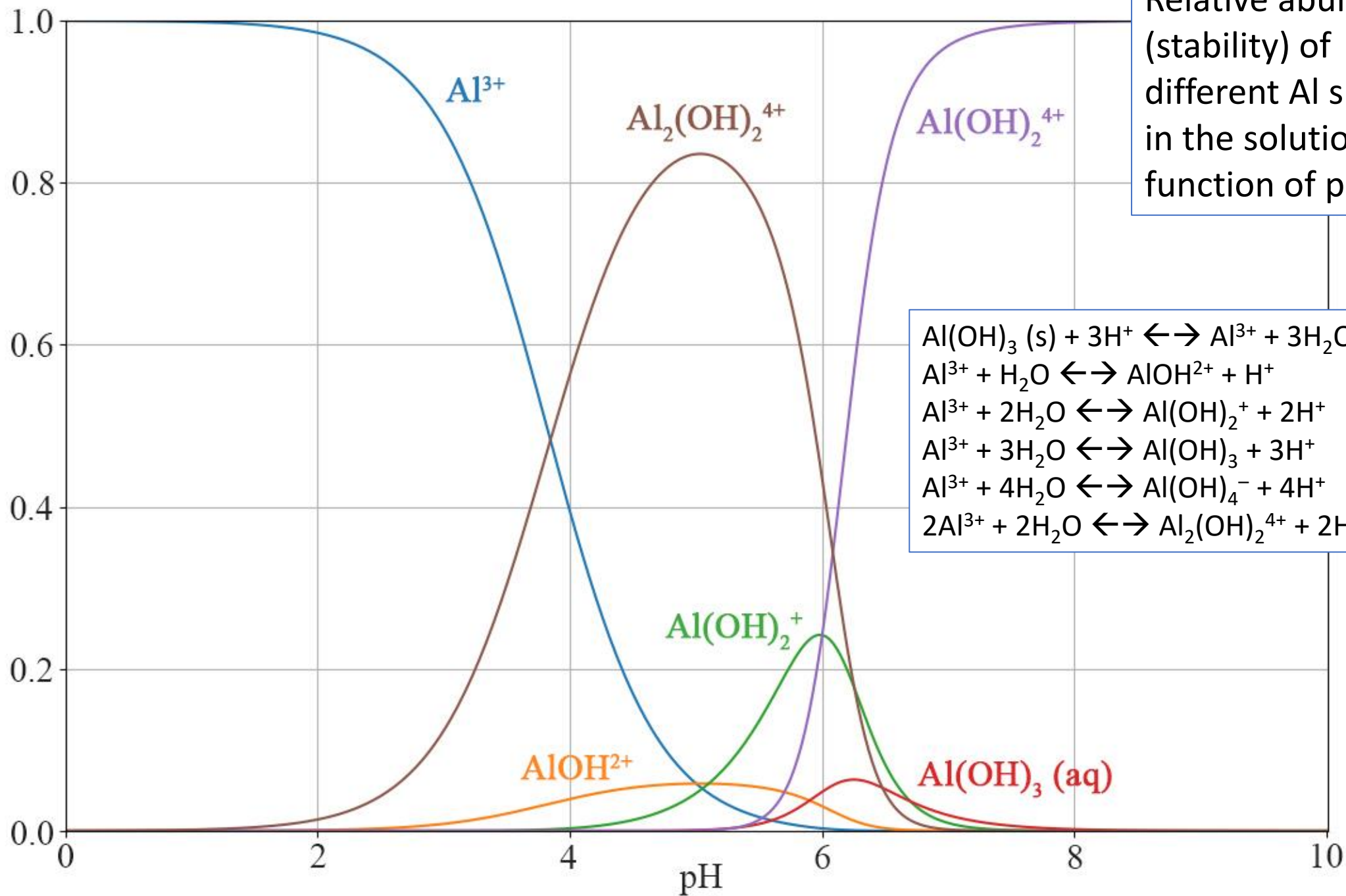
Al^{3+}

if pH > 5 $[\text{Al}(\text{OH})]^{2+}$ and $[\text{Al}(\text{OH})_2]^+$ are stable

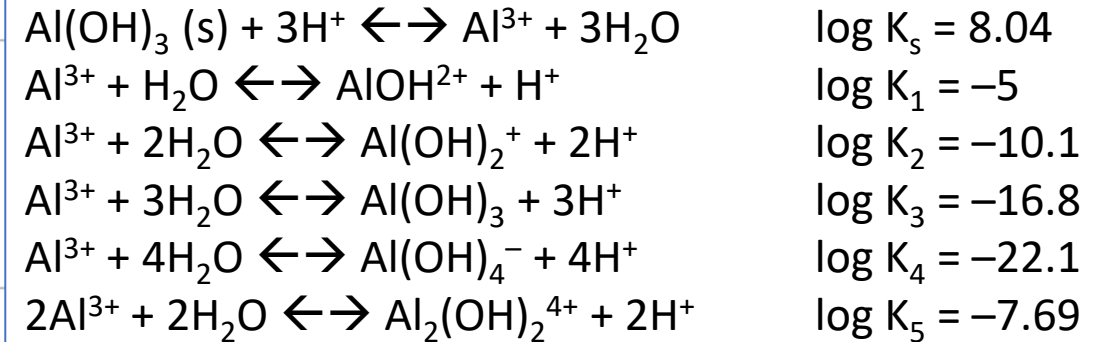
if pH is neutral → formation of $\text{Al}(\text{OH})_3$, in slightly alkaline conditions → $[\text{Al}(\text{OH})_4]^-$

as the concentration of Al increases so called polynuclear forms are formed

$[\text{AlO}_4\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12}]^{7+}$ (toxic forms of Al are **highlighted**)

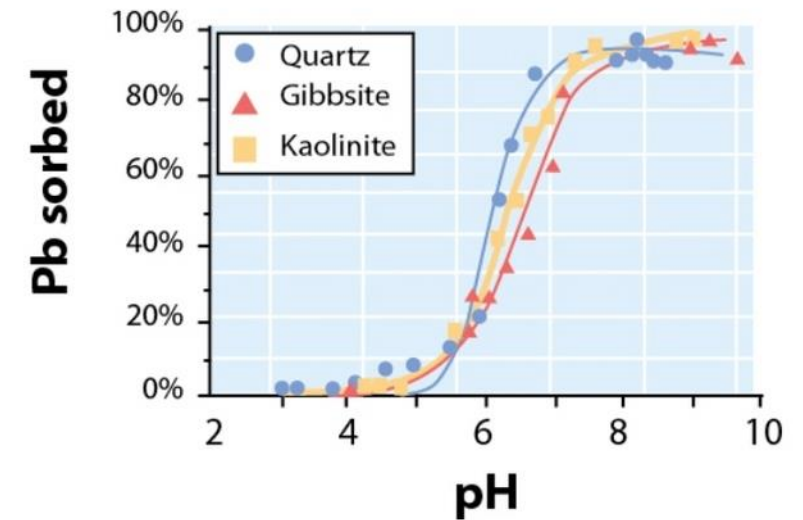
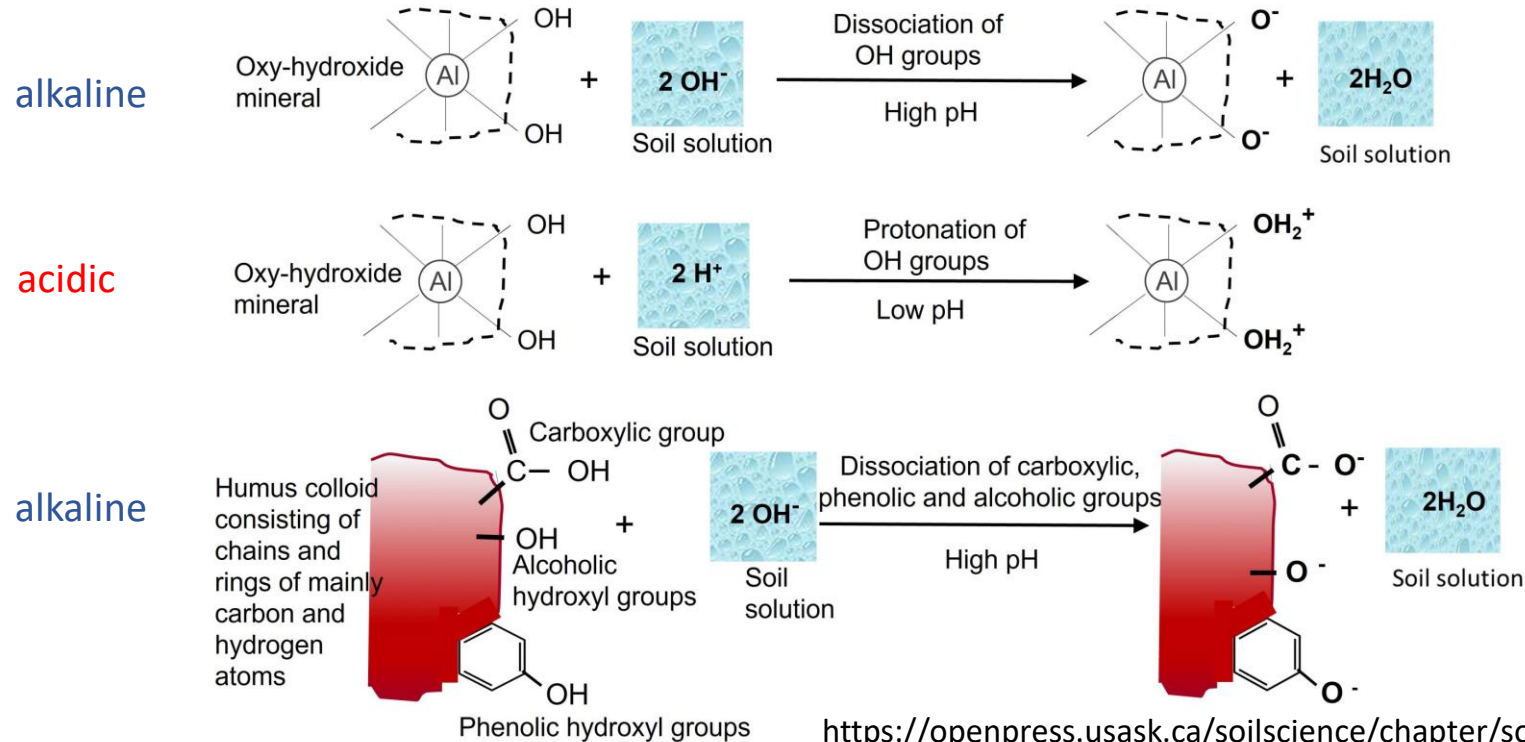


Relative abundance
(stability) of
different Al species
in the solution as a
function of pH



Negative consequences of soil acidity (mobility and toxicity of risk elements)

- mobility and availability of risk elements that are present in soils in form of cations (Cd, Pb, Ni, Co, Hg, Cu) increases with lowering of pH
- on the other hand, in case of elements that are in anionic form (As, Mo, Sb) their mobility is higher in neutral or alkaline pH
- in acid conditions soil colloids show positive charge (limited sorption of cations); on contrary, if pH values are higher → functional groups in soil colloids are dissociated → negative charge → sorption of cations increases

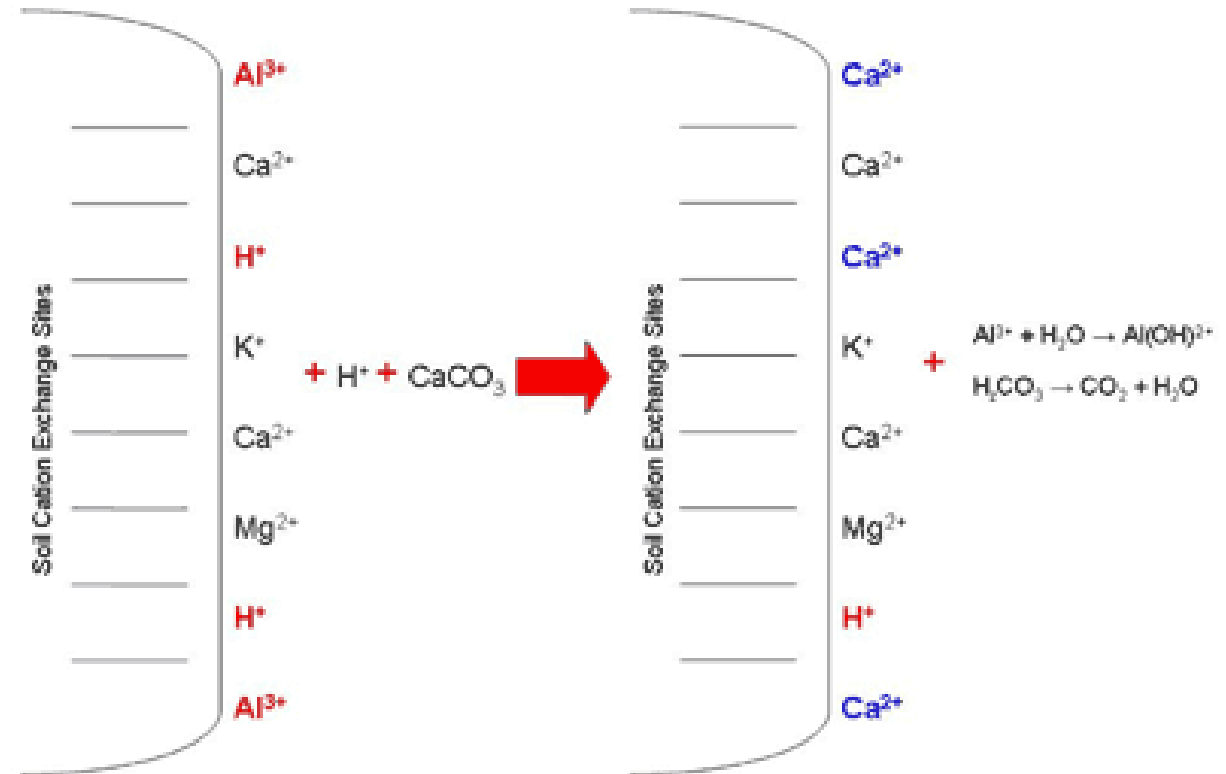


<https://www.nature.com/scitable/knowledge/library/introduction-to-the-sorption-of-chemical-constituents-94841002/>

<https://openpress.usask.ca/soilscience/chapter/soil-chemistry/>

Amelioration of acidic soils (liming)

- relatively non-expensive materials
- the main component that causes neutralization is calcite mineral and its dissolution
 $\text{CaCO}_3 + \text{H}_2\text{O} \rightarrow \text{Ca}^{2+} + \text{HCO}_3^- + \text{OH}^-$
- general form of equation that expresses interaction of calcite with soil (containing Al):
 $2\text{Al-soil} + 3\text{CaCO}_3 + 3\text{H}_2\text{O} \rightarrow 3\text{Ca-soil} + 2\text{Al}(\text{OH})_3 + 3\text{CO}_2$
- frequency of liming depends on various factors (**soil parent material, annual precipitation rate, hydraulic conductivity and permeability of soil**)
- it ranges, once per year – once per decade (depending on mentioned factors)



$$\text{Lime rate}(\text{Mg ha}^{-1}) = 1.8 \left[\frac{\text{Al}^{3+} - \text{TAS}(\text{Al}^{3+} + \text{Ca}^{2+} + \text{Mg}^{2+})}{100} \right]$$

Al, Ca, and Mg are exchangeable cations extracted with a neutral unbuffered salt
 TAS is the %Al saturation tolerated by the crop or cultivar