This paper discusses alkaline-sodic soils and acid-sulphate soils. R.J.Oosterbaan, March 2003 On website https://www.waterlog.info public domain, latest upload 20-11-2017

Lecture note International Course on Land Drainage (ICLD) International Institute for Land Reclamation and Improvement (ILRI) Wageningen, The Netherlands

I. SOIL ALKALINITY (Alkaline-sodic soils)

Definition

Alkaline soils are soils (mostly clay soils) with a high pH (> 9) and a poor soil structure and a low infiltration capacity. They are not saline, i.e. the total amount of soluble soils, especially sodium chlorides, is not excessive (ECe < 4 to 8 dS/m). Often they have a hard calcareous layer at 0.5 to 1 m. depth.

Causes

The causes of soil alkalinity are natural or they can be man-made. The natural development is due to the presence soil minerals producing sodium carbonate upon whethering. The man-made development is due to the application of irrigation water (surface or ground water) containg a relatively high proportion of sodium bicarbonates)

Where

The extent of alkaline soils is not precisely known. Important research on alkaline soils has mainly occurred in Central Europe and North India (above the Ganges river), where alkaline soils occur frequently.

Problems

Alkaline soils are difficult to take into agricultural production. Rainwater stagnates on the soil easily and, in dry periods, irrigation is hardly possible. Agriculture is limited to crops tolerant to surface water logging (e.g. rice, grasses) and the productivity is low.

Details

Soil alkalinity is associated with the presence of sodium carbonates (Na_2CO_3) in the soil, either as a result of natural mineralization of the soil particles or brought in by irrigation and/or floodwater. The sodium carbonate, when dissolved in water, dissociates into $2Na^+$ (two sodium cations, i.e. ions with a positive electric charge) and CO_3^{--} (a carbonate anion, i.e. an ion with a - double - negative electric charge).

The sodium-carbonate can react with water to produce carbon-dioxide (CO_2) , escaping as a gas, and sodium-hydroxide (Na^+OH^-) , which is alkaline and gives high pH values (pH>10). To understand this reaction, we may consider the water (H_2O) as being partly dissociated into H^+ (hydrogen) and OH^-

(hydroxyl) ions. In pure, neutral water, the concentration of $\rm H^+$ and $\rm OH^-$ ions equals $10^{-0.7}$ eq/l each (respectively 10^{-7} g/l and 17×10^{-7} g/l), a very small concentration.

The pH, being the negative log value of the H^+ concentration in eq/l, is 7. Similarly, the pOH is also 7.

Please note that each unit decrease in pH indicates a tenfold increase of the H^+ concentration. Similarly, each unit increase in pH indicates a tenfold increase of the OH⁻ concentration.

In water with dissolved salts, the concentrations of the $\rm H^+$ and $\rm OH^-$ ions may change, but the sum of pH and pOH remains equal to 14.

Water with excess H^+ ions is called acid (pH < 6), and water with excess OH^- ions is called alkaline (pH > 8). Soil moisture with pH < 4 is called very acid and with pH > 10 very alkaline.

The reaction between Na_2CO_3 and H_2O can represented as follows:

 $2Na^{+} + CO_{3}^{--} + 2H^{+} + 2OH^{-} --> 2Na^{+} + 2OH^{-} + H_{2}CO_{3}$

The acid H_2CO_3 is unstable and produces H_2O and CO_2 (carbon dioxide gas, escaping into the atmosphere). This explains the remaining <u>alkalinity</u> in the form of soluble sodium hydroxide.

Not all sodium carbonate follows the above chemical reaction. The remaining sodium carbonate, and hence the presence of CO_3^{--} ions, causes $CaCO_3$ (which is only slightly soluble) to precipitate as solid calcium carbonate (limestone). Hence, the calcium ions Ca^{++} are immobilized:

 $2Na^{+} + CO_{3}^{--} + Ca^{++} --> 2Na^{+} + CaCO_{3}$ (solid)

The presence of abundant Na^+ ions and the precipitation of Ca^{++} ions causes the clay particles, which have negative electric charges along their surfaces, to adsorb more Na^+ and, in exchange, release Ca^{++} , by which their exchangeable sodium percentage (ESP) is increased as follows:



Clay particles with considerable ESP (> 16), in non-saline conditions, and in contact with non-saline water occupy a larger volume than otherwise, because the Na⁺ ions are quite mobile and have smaller electric charges than Ca⁺⁺ ions, hence they are adsorbed less coherently to the surface of the clay particle and they float farther away: the soil swells.

The phenomenon is called <u>sodicity</u> and results in deterioration of the soil structure, and especially crust formation and compaction of the top layer.

Hence the infiltration capacity of the soil and the water availability in the soil is reduced, whereas the surface-water-logging or runoff is increased. Seedling emergence and crop production are badly affected.

Under saline conditions, the many ions in the soil solution counteract the swelling of the soil.

Certain clay minerals with 100% ESP (i.e. fully sodium saturated) are called bentonite which is used in civil engineering to place impermeable curtains in the soil, e.g. below dams, to prevent seepage of water.

The problems of alkalinity and sodicity go hand in hand. Alkaline/sodic soils are not necessarily saline, and the alkalinity problem is worse as the salinity is less. Alkalinity problems are more pronounced in clay soils than in loamy, silty or sandy soils. The clay soils containing montmorrillonitic or smectitic minerals (swelling clays) are more subject to alkalinity problems than illitic or kaolinitic clay soils. The reason is that the former types of clay have larger specific surface areas (i.e. the surface area of the soil particles divided by their volume).

Solutions

Alkaline/sodic soils with solid $CaCO_3$ can be reclaimed with grass cultures, ensuring the incorporation of much acidifying organic material into the soil, and leaching of the excess sodium. Deep ploughing and incorporating the calcareous subsoil into the topsoil also helps.

It is also possible to reclaim alkaline soils by adding acidifying minerals like pyrite (see next section on acid sulphate soils).

If necessary, gypsum (calcium sulphate, $\text{CaSO}_4)$ can also be applied as a source of $\text{Ca}^{\text{++}}$ ions.

To reclaim the soils properly one needs prohibitively high of doses of amendments. Most efforts are therefore directed to improving the top layer only (say the first 10 cm of the soils), as the top layer is most sensitive to structure deterioration. The treatments, however, need to be repeated in a few (say 5) years time

It will be important to refrain from irrigation with poor quality water.

The quality of the irrigation water in relation to the alkalinity hazard is expressed by the following two indices:

1) The sodium adsorption ratio (SAR)

SAR = $\frac{[Na^{+}]}{\sqrt{[Ca^{++}/2 + Mg^{++}/2]}} = \frac{\{Na^{+}/23\}}{\sqrt{\{Ca^{++}/40 + Mg^{++}/24\}}}$

where: [] stands for concentration in meq/l, and
{} stands for concentration in mg/l.

It is seen that Mg (Magnesium) is thought to play a similar role as the Calcium.

The SAR should not be much higher than 20 and preferably less than 10;

When the soil has been exposed to water with a certain SAR value for some time, the ESP value tends to become about equal to the SAR value.

2) The residual sodium carbonate content (RSC, meq/1):

RSC =
$$[HCO_{3}^{-} + CO_{3}^{-}] - [Ca^{++} + Mg^{++}]$$

= $\{HCO_{3}^{-}/61 + CO_{3}^{-}/30\} - \{Ca^{++}/20 + Mg^{+}/12\}$

which must not be much higher than 1 and preferably less than 0.5.

Note that the above expression recognises the presence of bi-carbonates (HCO_3^{-}) , the form in which most carbonates are dissolved. For simplicity reasons, this was not considered in the foregoing explanations.

Comment

Saline soils are mostly also sodic (the predominant salt is sodium chloride) but not very alkaline. However, upon leaching they are usually converted into non-sodic soils as the Na⁺ ions are easily removed. Therefore, the sodic problem is more acute in non-saline sodic soils, and mostly they do not need gypsum applications. (See also the Chacupe case study: www.waterlog.info/pdf/acidalka.pdf).

A good treatise on alkaline-sodic soils can be in Chhabra (1996), see list of references.

II. SOIL ACIDITY (Acid-sulphate soils)

Definition

Acid sulphate are drained coastal wetland soils that have become acid (pH<4) due to oxidation of the pyritic minerals in the soil. Undrained soils containing pyrites need not be acid and they are called potential acid sulphate soils.

Causes

The cause of the formation of acid sulphate soils is the drainage and flood control effectuated to permit agricultural or sedentary activities.

Where

(Potential) Acid sulphate soils are found coastal lowlands, especially in the (semi) humid tropics, but not exclusively. In the tropics the soils are often related to mangrove vegetations under tidal influence. The soils are found extensively in South-East Asia, West Africa, and North-East South-America, but also in other regions.

Problems and solutions

Acid sulphate soils are unproductive. The lands look barren and the water is very clear, devoid of silt and life. The soils can be colourful.

Indigenous populations have managed to develop acid sulphate soils, e.g. for rice cultivation. It has taken them many years of careful management and toil (Oosterbaan 1981). The soils are hardly attractive for large scale and commercial exploitation. However, there have been efforts in that direction at deplorable loss of environmental quality and of financial resources. The best cure would be to restore the original conditions (see table further on). Unfortunately most undertakers are not interested to spend additional funds in repairing of what was damaged already at a large expense.

The indigenous efforts have led to soils that are no longer acid due to long lasting drainage and removal of the acids. These soils have acquired an excellent and stable soil structure coupled with a high permeability. Their fertility, however, has gone. Continued cultivation requires frequent application of organic manure and fertilizers.

In tropical humid climates with high rainfall rice yields in acid coastal lowlands can benefit from restricted subsurface drainage during a short time (< 1 month) in a relatively dry period (Oosterbaan 1992).

Details

When draining pyrite (FeS₂) containing soils (also called cat-clays), the soil may become extremely acid (pH < 4) due to oxidation (reaction with oxygen, O_2 , gas) of pyrite into sulphuric acid (H₂SO₄), giving acid sulphate soils. In its simplest form, the chemical reaction is:

 $2FeS_2 + 9O_2 + 4H_2O \longrightarrow 8H^+ + 4SO_4^- + 2Fe(OH)_3$ (solid)

The product $Fe(OH)_3$, iron (III) hydroxide (orange), precipitates as a solid, insoluble mineral, by which the alkalinity is immobilized and the acidity remains active. In alkaline soils, in contrast, it is the escape of CO_2 gas and the precipitation of $CaCO_3$ that causes the removal of acidity from the system whereby the alkalinity remains active.

The process of acidification is accompanied by the formation of high amounts of aluminium $(Al^{+++} \text{ ions}, \text{ released from clay minerals under influence})$ of the acidity), which are harmful to the crop.

Other products of the chemical reactions are:

H ₂ S	hydrogen sulphide, a smelly gas;									
S	sulphur (yellow)									
FeS	iron (II) sulphide (black/grey/blue)									
Fe ₂ O ₃	(haematite, iron (III) oxide, red coloured)									
Fe0.OH	goethite (brown)									
Fe Compounds	(e.g. jarosite, yellow)									
H-Clay	(hydrogen clay with a large fraction of adsorbed $\ensuremath{\textsc{H}^{\scriptscriptstyle +}}$ ions,									
	a stable mineral, but poor in nutrients).									

It can be seen that the iron can be present in bi-valent (II) and tri-valent (III) forms (Fe⁺⁺, the ferro ion, and Fe⁺⁺⁺, the ferri ion respectively). The ferro form is soluble, whereas the ferri form is not. The more oxidised the soil becomes, the more the ferri forms will dominate.

Acid sulphate soils exhibit an array of colours ranging from black, to brown, blue-grey, red, orange and yellow.

The hydrogen clay can be improved by admitting sea water: the Mg and Na present in the sea water will replace the hydrogen adsorbed.

Cat-clays occur mainly in coastal lowland (Beek et al. 1980) and are often not cultivated or, if they are, planted under rice, so that the soil can be kept wet preventing oxidation. Subsurface drainage of these soils is normally not advisable. However, cultivated acid sulphate soils can often not be kept wet continuously because of climatic dry spells and shortages of irrigation water. In such a situation, surface drainage may help to remove the acidic and toxic chemicals (formed in the dry spells) during rainy periods. On the long run surface drainage can help to reclaim acid sulphate soils (Oosterbaan 1981). In the short run, careful and restricted use of subsurface drainage in humid climates can help to improve rice yields (Oosterbaan 1992).

For additional information reference is made to Dent (1986). See also the following table.

Drainage and yield of Malaysian oil palm on acid sulphate soils (after Toh Peng Yin and Poon Yew Chin 1982)

		yi	eld in	n to	ns o	f fr	esh f:	ruit	per	ha		
year :	60	61	62a)	63	64	65	66b)	67	68	69	70	71
yield:	17	14	15	12	8	2	4	8	14	19	18	19

a) drainage depth and intensity increased

b) water table raised again to counter negative effects of a)

Note that subsurface drainage can be harmful, but that soils can recover after reducing drainage again.

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This article can be downloaded from www.waterlog.info/pdf/caution.pdf In example 4 it discusses the successful application of subsurface drainage in acid sulphate soils in coastal polders of Kerala state, India.

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