

SOIL CHEMISTRY: A REVIEW

Nachiket S Dighe¹, Shashikant R Pattan¹, Deepak S Musmade¹, Vinayak M Gaware¹, Mangesh B Hole¹, Ramesh S Kalkotwar¹ and Santosh R Butle²

1. Department of Pharmaceutical Chemistry, Pravara Rural College Of Pharmacy, Pravaranagar, M.S, India

2. Department of Pharmaceutical Chemistry, University Department SRTM, Nanded, M.S.India

Summary

The study of chemical characteristics of a soil will helps us to overcome the problems arised in soil. Specially the one which are related to the acidity, alkalinity of the soil. It also helps us to maintain the desired p^H of soil which is prerequisite for increasing the productivity of the soil. The use of carbon cycle, sulphur cycle and Phasphorus cycle will helps in identifying the nature and importance of the manures which contains it in the large amount of these essential elements.

Key-Words: Carbon cycle, Phosphorus cycle , Regulatory framework, Soil chemistry etc.

Address for correspondence:

Mr. Nachiket S Dighe

Assistant Professor & HOD, Department of Pharmaceutical Chemistry,

Pravara Rural College of Pharmacy, Pravaranagar

A/P- Loni Bk. Taluka -Rahata, Dist-Ahmednagar 413736,

India (MS). E mail-nachiket1111@rediffmail.com

Introduction

Soil chemistry is the study of the chemical characteristics of soil. Soil chemistry is affected by mineral composition, organic matter and environmental factors.

History¹

Until the late 1960s, soil chemistry focused primarily on chemical reactions in the soil that contribute to pedogenesis or that affect plant growth. Since then concerns have grown about environmental pollution, organic and inorganic soil contamination and potential ecological health and environmental health risks. Consequently, the emphasis in soil chemistry has shifted from pedology and agricultural soil science to an emphasis on environmental soil science.

Environmental soil chemistry

A knowledge of environmental soil chemistry is paramount to predicting the fate, mobility and potential toxicity of contaminants in the environment. The vast majority of environmental contaminants are initially released to the soil. Once a chemical is exposed to the soil environment a myriad of chemical reactions can occur that may increase or decrease contaminant toxicity. These reactions include adsorption/desorption, precipitation, polymerization, dissolution, complexation and oxidation/reduction. These reactions are often disregarded by scientists and engineers involved with environmental remediation. Understanding these processes enable us to better predict the fate and toxicity of contaminants and provide the knowledge to develop scientifically correct, and cost-effective remediation strategies.

Concepts

Anion and cation exchange capacity, Soil pH, Mineral formation and transformation processes
Clay mineralogy, Sorption and precipitation reactions in soil, Oxidation-reduction reactions,
Chemistry of problem soils

Acid sulfate soil

Acid sulfate soils are naturally occurring soils, sediments or organic substrates (e.g. peat) that are formed under waterlogged conditions. These soils contain iron sulfide minerals (predominantly as the mineral pyrite) or their oxidation products. In an undisturbed state below the water table, acid sulfate soils are benign. However if the soils are drained, excavated or exposed to air by a lowering of the water table, the sulfides will react with oxygen to form sulfuric acid.² Release of this sulfuric acid from the soil can in turn release iron, aluminium, and other heavy metals (particularly arsenic) within the soil. Once mobilized in this way, the acid and metals can create a variety of adverse impacts: killing vegetation, seeping into and acidifying groundwater and water bodies, killing fish and other aquatic organisms, and degrading concrete and steel structures to the point of failure.²

Acid sulfate soil formation



Figure 1: Polders with acid sulfate soils in Guinea Bissau along a sea-arm amidst mangroves

The soils and sediments which are most prone to becoming acid sulfate soils are those which formed within the last 10,000 years, after the last major sea level rise. When the sea level rose and inundated the land, sulfate in the seawater mixed with land sediments containing iron oxides and organic matter.² Under these anaerobic conditions, lithotrophic bacteria such as *Desulfovibrio desulfuricans* form iron sulfides (pyrite).² Up to a point, warmer temperatures are more favourable conditions for these bacteria, creating a greater potential for formation of iron sulfides. Tropical waterlogged environments, such as mangrove swamps or estuaries, may contain higher levels of pyrite than those formed in more temperate climates.³ The pyrite is stable until it is exposed to air, at which point the pyrite oxidises and produces sulfuric acid. The impacts of acid sulfate soil leachate may persist over a long time, and/or peak seasonally (after dry periods with the first rains). In some areas of Australia, acid sulfate soils that drained 100 years ago are still releasing acid.³

Chemical reaction

When drained, pyrite (FeS₂) containing soils (also called cat-clays) may become extremely acidic (pH < 4) due to the oxidation of pyrite into sulfuric acid (H₂SO₄). In its simplest form, this chemical reaction is as follows:

$$2 \text{FeS}_2 + 9 \text{O}_2 + 4 \text{H}_2\text{O} \rightarrow 8 \text{H}^+ + 4 \text{SO}_4^{2-} + 2 \text{Fe}(\text{OH})_3 \text{ (solid)}$$
⁴ The product Fe(OH)₃, iron(III) hydroxide (orange), precipitates as a solid, insoluble mineral by which the alkalinity component is immobilized, while the acidity remains active in the sulfuric acid. The process of acidification is accompanied by the formation of high amounts of aluminium (Al³⁺, released from clay minerals under influence of the acidity), which are harmful to vegetation. Other products of the chemical reaction are:

Hydrogen sulfide (H₂S), a smelly gas, Sulfur (S), a yellow solid, Iron(II) sulfide (FeS), a black/gray/blue solid, Haematite (Fe₂O₃), a red solid, Goethite (FeO.OH), a brown mineral, Schwertmannite a brown mineral, Iron sulfate compounds (e.g. jarosite), H-Clay (hydrogen clay, with a large fraction of adsorbed H⁺ ions, a stable mineral, but poor in nutrients). The iron can be present in bivalent and trivalent forms (Fe²⁺, the ferrous ion, and Fe³⁺, the ferric ion respectively). The ferrous form is soluble, whereas the ferric form is not. The more oxidized the soil becomes, the more the ferric forms will dominate.

Impacts of acid sulfate soil

Disturbing potential acid sulfate soils can have a destructive effect on plant and fish life, and on coastal ecosystems. Flushing of acidic leachate to groundwater and surface waters can cause a number of impacts, including [3] Ecological damage to aquatic and riparian ecosystems through fish kills, increased fish disease outbreaks, dominance of acid-tolerant species, precipitation of iron, etc. Effects on estuarine fisheries and aquaculture projects (increased disease, loss of spawning area, etc). Contamination of groundwater with arsenic, aluminium and other heavy metals. Reduction in agricultural productivity through metal contamination of soils (predominantly by aluminium). Damage to infrastructure through the corrosion of concrete and steel pipes, bridges and other sub-surface assets.

Agricultural impacts



Figure 2: Agricultural impacts

Sea water is admitted to a bunded polder on acid sulfate soil for soil improvement and weed control, Guinea Bissau Potentially acid sulfate soils (also called cat-clays) 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. The crop yields were modest, but provided enough income to make a decent living. Reclaimed acid sulfate soils have a well developed soil structure, they are well permeable, but infertile due to the leaching that has occurred. In the second half of the 20th century, in many parts of the world, waterlogged and potentially acid sulfate soils have been drained aggressively to make them productive for agriculture. The results were disastrous.⁵ The soils are unproductive, the lands look barren and the water is very clear, devoid of silt and life. The soils can be colorful, though.

Construction

When brickwork is persistently wet, as in foundations, retaining walls, parapets and chimneys, sulfates in bricks and mortar may in time crystallise and expand and cause mortar and renderings to disintegrate. Adequate protection can exist using a polythene sheeting to encase the foundations or using a sulfate resistant Portland cement. To identify the pH level of the ground a soil investigation must take place.

Acid sulfate soil restoration

By raising the water table, after damage has been inflicted due to over-intensive drainage, the soils can be restored. The following table gives an example. Drainage and yield of Malaysian oil palm on acid sulfate soils (after Toh Peng Yin and Poon Yew Chin, 1982)

Year	60	61	62	63	64	65	66	67	68	69	70	71
Yield	17	14	15	12	8	2	4	8	14	19	18	19

Table no:1:Yield in tons of fresh fruit per ha

Drainage depth and intensity were increased in 1962. The water table was raised again in 1966 to counter negative effects.

Alkali soils

Alkali, or alkaline, soils are clay soils with high pH (> 9), a poor soil structure and a low infiltration capacity. Often they have a hard calcareous layer at 0.5 to 1 m. depth (in India this layer is called 'kankar'). Alkali soils owe their unfavorable physico-chemical properties mainly to the dominating presence of sodium carbonate which causes the soil to swell. They derive their name from the alkali metal group of elements to which the sodium belongs and that can induce basicity. Sometimes these soils are also referred to as (alkaline) sodic soils.

Causes

The causes of soil alkalinity are natural or they can be man-made. The natural cause is the presence of soil minerals producing sodium carbonate (Na_2CO_3) upon weathering. The man-made cause is the application of irrigation water (surface or ground water) containing a relatively high proportion of sodium bicarbonates.

Occurrence

The extent of alkaline soils is not precisely known.⁷

Agricultural problems

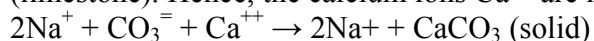
Alkaline soils are difficult to take into agricultural production. Due to the low infiltration capacity, rain water stagnates on the soil easily and, in dry periods, irrigation is hardly possible. Agriculture is limited to crops tolerant to surface waterlogging (e.g. rice, grasses) and the productivity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

Chemistry

Soil alkalinity is associated with the presence of sodium carbonates or (soda) (Na_2CO_3) in the soil,⁸ either as a result of natural weathering of the soil particles or brought in by irrigation and/or flood water. The sodium carbonate, when dissolved in water, dissociates into 2Na^+ (two sodium cations, i.e. ions with a positive electric charge) and CO_3^{2-} (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 (or rather basic) and gives high pH values ($\text{pH} > 9$). [8] Water (H_2O) is partly dissociated into H^+ (hydrogen) and OH^- (hydroxyl) ions. The ion H^+ has a positive electric charge (+) and the hydroxyl group OH^- has a negative charge (-). In pure, neutral water, the concentration of H^+ and OH^- ions equals 10^{-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. 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 H^+ and OH^- ions may change, but the sum of pH and pOH remains equal to $7 + 7 = 14$. Water with excess H^+ ions is called acid ($\text{pH} < 6$), and water with excess OH^- ions is called alkaline or rather basic ($\text{pH} > 8$). Soil moisture with $\text{pH} < 4$ is called very acid and with $\text{pH} > 10$ very alkaline (basic). The reaction between Na_2CO_3 and H^+O can be represented as follows:



The acid H_2CO_3 is unstable and produces H_2O (water) and CO_2 (carbon dioxide gas, escaping into the atmosphere). This explains the remaining alkalinity (or rather basicity) in the form of soluble sodium hydroxide and the high pH or low pOH. Not all sodium carbonate follows the above chemical reaction. The remaining sodium carbonate, and hence the presence of CO_3^{2-} ions, causes CaCO_3 (which is only slightly soluble) to precipitate as solid calcium carbonate (limestone). Hence, the calcium ions Ca^{++} are immobilized:



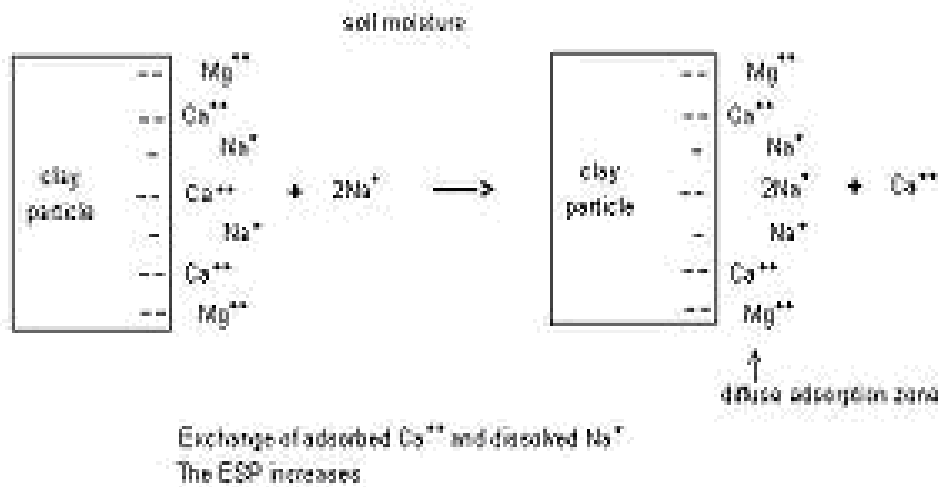


Figure 3: Soil Alkalinity

Sodium exchange process between clay particles and the soil moisture. The presence of abundant Na^+ ions in the soil solution and the precipitation of Ca^{++} ions as a solid mineral causes the clay particles, which have negative electric charges along their surfaces, to adsorb more Na^+ in the diffuse adsorption zone (DAZ, see figure, officially called diffuse double layer⁹ and, in exchange, release Ca^{++} , by which their exchangeable sodium percentage (ESP) is increased as illustrated in the figure. Na^+ is more mobile and has a smaller electric charge than Ca^{++} so that the thickness of the DAZ increases as more sodium is present. The thickness is also influenced by the total concentration of ions in the soil moisture in the sense that higher concentrations cause the DAZ zone to shrink. Clay particles with considerable ESP (> 16), in contact with non-saline soil moisture have an expanded DAZ zone and the soil swells (dispersion).⁹ The phenomenon 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, so that saline soils usually do not have unfavorable physical properties. Alkaline soils, in principle, are not saline since 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.

Solutions

Alkaline 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.⁹ Deep plowing and incorporating the calcareous subsoil into the top soil also helps. It is also possible to reclaim alkaline soils by adding acidifying minerals like pyrite. Alternatively, gypsum (calcium sulfate, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) can also be applied as a source of Ca^{++} ions to replace the sodium at the exchange complex.⁹ There must be enough natural drainage to the underground, or else an artificial subsurface drainage system must be present, to permit leaching of the excess sodium by percolation of rain and/or irrigation water through the soil profile. To reclaim the soils completely one needs prohibitively high 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 deterioration of the soil structure.⁹ 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.

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

where: [] stands for concentration in milliequivalents/liter (briefly meq/l), and { } stands for concentration in mg/l.

It is seen that Mg (Magnesium) is thought to play a similar role as Ca (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 (RSC, meq/l)

The formula for calculating residual sodium carbonate is:

$$\text{RSC} = [\text{HCO}_3^- + \text{CO}_3^{--}] - [\text{Ca}^{++} + \text{Mg}^{++}]$$

$$= \{\text{HCO}_3^-/61 + \text{CO}_3^{--}/30\} - \{\text{Ca}^{++}/20 + \text{Mg}^{++}/12\}$$

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

The above expression recognizes the presence of bicarbonates (HCO₃⁻), the form in which most carbonates are dissolved.

Leaching saline sodic soils

Saline soils are mostly also sodic (the predominant salt is sodium chloride), but they do not have a very high pH nor a poor infiltration rate. Upon leaching they are usually not converted into a (sodic) alkali soil as the Na⁺ ions are easily removed. Therefore, saline (sodic) soils mostly do not need gypsum applications for their reclamation.⁹

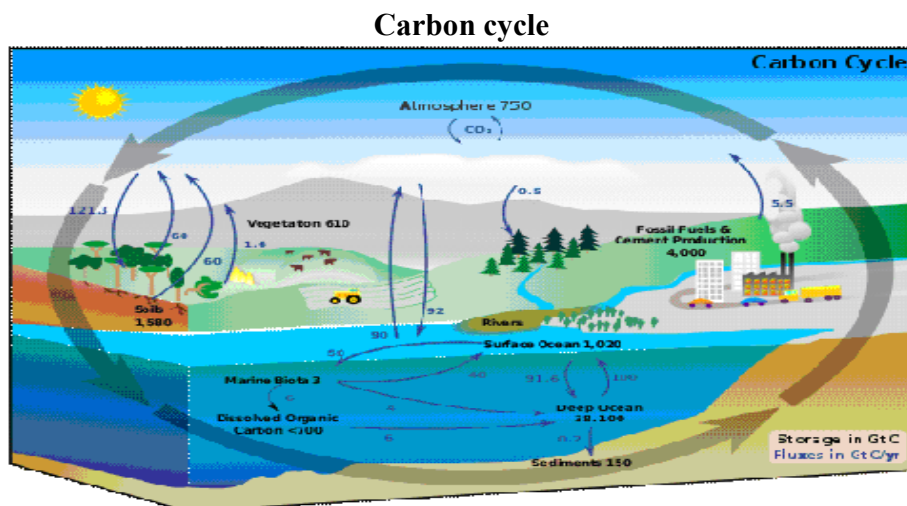


Figure 4: Carbon Cycle

The **carbon cycle** is the biogeochemical cycle by which carbon is exchanged among the biosphere, pedosphere, geosphere, hydrosphere, and atmosphere of the Earth. It is one of the most important cycles of the earth and allows for the most abundant element to be recycled and reused throughout the biosphere and all of its organisms. The carbon cycle is usually thought of as five major reservoirs of carbon interconnected by pathways of exchange. These reservoirs are: The atmosphere The terrestrial biosphere, which is usually defined to include fresh water systems and non-living organic material, such as soil carbon. The oceans, including dissolved inorganic carbon and living and non-living marine biota, The sediments including fossil fuels. The earth's interior, carbon from the earth's mantle and crust is released to the atmosphere and hydrosphere by volcanoes and geothermal systems. The annual movements of carbon, the carbon exchanges between reservoirs, occur because of various chemical, physical, geological, and biological processes. The ocean contains the largest active pool of carbon near the surface of the Earth, but the deep ocean part of this pool does not rapidly exchange with the atmosphere. The global carbon budget is the balance of the exchanges (incomes and losses) of carbon between the carbon reservoirs or between one specific loop (e.g., atmosphere ↔ biosphere) of the carbon cycle. An examination of the carbon budget of a pool or reservoir can provide information about whether the pool or reservoir is functioning as a source or sink for carbon dioxide.

In the atmosphere

Forests store 86% of the planet's above-ground carbon and 73% of the planet's soil carbon.¹⁰ At the surface of the oceans towards the poles, seawater becomes cooler and more carbonic acid is formed as CO₂ becomes more soluble. This is coupled to the ocean's thermohaline circulation which transports dense surface water into the ocean's interior (see the entry on the solubility pump). In upper ocean areas of high biological productivity, organisms convert reduced carbon to tissues, or carbonates to hard body parts such as shells and tests. These are, respectively, oxidized (soft-tissue pump) and redissolved (carbonate pump) at lower average levels of the ocean than those at which they formed, resulting in a downward flow of carbon (see entry on the biological pump). The weathering of silicate rock (see Carbonate-Silicate Cycle). Carbonic acid reacts with weathered rock to produce bicarbonate ions. The bicarbonate ions produced are carried to the ocean, where they are used to make marine carbonates. Unlike dissolved CO₂ in equilibrium or tissues which decay, weathering does not move the carbon into a reservoir from which it can readily return to the atmosphere. In 1850, atmospheric carbon dioxide was about 280 parts per million (ppm), and today it is about 385ppm.¹⁰ Future CO₂ emission can be calculated by the Kaya identity.

Carbon is released into the atmosphere in several ways:

Through the respiration performed by plants and animals. This is an exothermic reaction and it involves the breaking down of glucose (or other organic molecules) into carbon dioxide and water. Through the decay of animal and plant matter. Fungi and bacteria break down the carbon compounds in dead animals and plants and convert the carbon to carbon dioxide if oxygen is present, or methane if not. Through combustion of organic material which oxidizes the carbon it contains, producing carbon dioxide (and other things, like water vapor). Burning fossil fuels such as coal, petroleum products, and natural gas releases carbon that has been stored in the geosphere for millions of years. Burning agrofuels also releases carbon dioxide which has been stored for only a few years or less. Production of cement. Carbon dioxide is released when limestone (calcium carbonate) is heated to produce lime (calcium oxide), a component of cement. At the

surface of the oceans where the water becomes warmer, dissolved carbon dioxide is released back into the atmosphere. Volcanic eruptions and metamorphism release gases into the atmosphere.

In the biosphere

The most important autotrophs for the carbon cycle are trees in forests on land and phytoplankton in the Earth's oceans. Photosynthesis follows the reaction $6\text{CO}_2 + 6\text{H}_2\text{O} \rightarrow \text{C}_6\text{H}_{12}\text{O}_6 + 6\text{O}_2$. Carbon is transferred within the biosphere as heterotrophs feed on other organisms or their parts (e.g., fruits). This includes the uptake of dead organic material (detritus) by fungi and bacteria for fermentation or decay. Most carbon leaves the biosphere through respiration. When oxygen is present, aerobic respiration occurs, which releases carbon dioxide into the surrounding air or water, following the reaction $\text{C}_6\text{H}_{12}\text{O}_6 + 6\text{O}_2 \rightarrow 6\text{CO}_2 + 6\text{H}_2\text{O}$. Otherwise, anaerobic respiration occurs and releases methane into the surrounding environment, which eventually makes its way into the atmosphere or hydrosphere (e.g., as marsh gas or flatulence). Burning of biomass (e.g. forest fires, wood used for heating, anything else organic) can also transfer substantial amounts of carbon to the atmosphere. Carbon may also be circulated within the biosphere when dead organic matter (such as peat) becomes incorporated in the geosphere. Animal shells of calcium carbonate, in particular, may eventually become limestone through the process of sedimentation. Much remains to be learned about the cycling of carbon in the deep ocean.

In the ocean

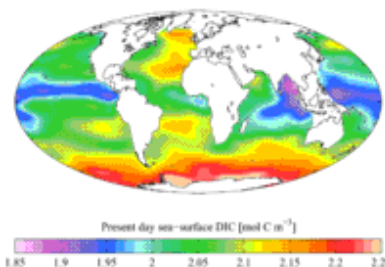
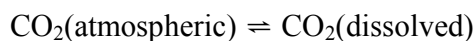


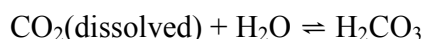
Figure 5: Carbon concentration in ocean

"Present day" (1990s) sea surface dissolved inorganic carbon concentration (from the GLODAP climatology) The oceans contain around 36,000 gigatonnes of carbon, mostly in the form of bicarbonate ion (over 90%, with most of the remainder being carbonate). Extreme storms such as hurricanes and typhoons bury a lot of carbon, because they wash away so much sediment. For instance, a team reported in the July 2008 issue of the journal *Geology* that a single typhoon in Taiwan buries as much carbon in the ocean—in the form of sediment—as all the other rains in that country all year long combined.¹² Inorganic carbon, that is carbon compounds with no carbon-carbon or carbon-hydrogen bonds, is important in its reactions within water. This carbon exchange becomes important in controlling pH in the ocean and can also vary as a source or sink for carbon. Carbon is readily exchanged between the atmosphere and ocean. In regions of oceanic upwelling, carbon is released to the atmosphere. Conversely, regions of downwelling transfer carbon (CO_2) from the atmosphere to the ocean. When CO_2 enters the ocean, it participates in a series of reactions which are locally in equilibrium:

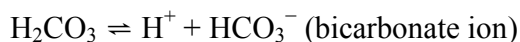
Solution:



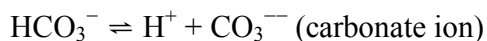
Conversion to carbonic acid:



First ionization:



Second ionization:



In the ocean the equilibria strongly favor bicarbonate. Since this ion is three steps removed from atmospheric CO_2 , the level of inorganic carbon storage in the ocean does not have a proportion of unity to the atmospheric partial pressure of CO_2 . The factor for the ocean is about ten: that is, for a 10% increase in atmospheric CO_2 , oceanic storage (in equilibrium) increases by about 1%, with the exact factor dependent on local conditions. This buffer factor is often called the "Revelle Factor", after Roger Revelle. In the oceans, carbonate can combine with calcium to form limestone (calcium carbonate, CaCO_3 , with silica), which precipitates to the ocean floor. Limestone is the largest reservoir of carbon in the carbon cycle. The calcium comes from the weathering of calcium-silicate rocks, which causes the silicon in the rocks to combine with oxygen to form sand or quartz (silicon dioxide), leaving calcium ions available to form limestone.¹⁴

Phosphorus cycle

The **phosphorus cycle** is the biogeochemical cycle that describes the movement of phosphorus through the lithosphere, hydrosphere, and biosphere. Unlike many other biogeochemical cycles, the atmosphere does not play a significant role in the movements of phosphorus, because phosphorus and phosphorus-based compounds are usually solids at the typical ranges of temperature and pressure found on Earth.

Phosphorus in the environment

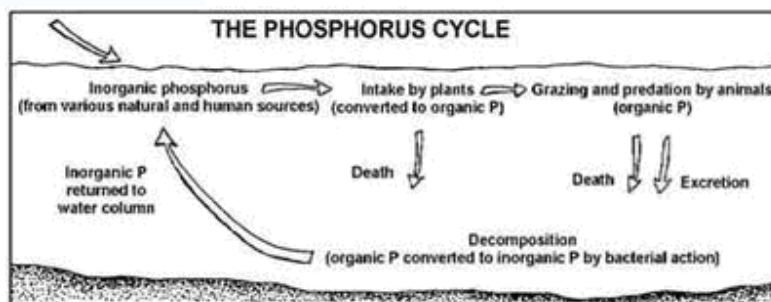


Figure 5: Phosphorus cycle

The aquatic phosphorus cycle

Phosphorus is an essential nutrient for plants and animals in the form of ions. Phosphorus forms parts of important life sustaining molecules but is not very common in the biosphere. Phosphorus does not enter the atmosphere, remaining mostly on land and in rock and soil minerals. 80 percent of the phosphorus is used to make fertilizers and a type of phosphorus such as dilute phosphoric acid is used in soft drinks. Phosphates may be effective in such ways but also causes pollution issues in lakes and streams. Over enrichment of phosphate can lead to algae bloom, because of the excess nutrients. This causes more algae to grow, bacteria consumes the algae and causes more bacteria to grow in large amounts. As rocks and sediments gradually wear down,

phosphate is released. In the atmosphere phosphorus is mainly small dust particles. Initially, phosphate weathers from rocks. The small losses in a terrestrial system caused by leaching through the action of rain are balanced in the gains from weathering rocks. In soil, phosphate is absorbed on clay surfaces and organic matter particles and becomes incorporated (immobilized). Plants dissolve ionized forms of phosphate. Herbivores obtain phosphorus by eating plants, and carnivores by eating herbivores. Herbivores and carnivores excrete phosphorus as a waste product in urine and feces. Phosphorus is released back to the soil when plants or animal matter decomposes and the cycle repeats.

Human interference

Human interference in the phosphorus cycle occurs by overuse or careless use of phosphorus fertilizers. This results in increased amounts of phosphorus as pollutants in bodies of water resulting in eutrophication. Eutrophication devastates water ecosystems.

Soil contamination



Figure 6: Soil Pollution

Soil pollution is caused by the presence of man-made chemicals or other alteration in the natural soil environment. This type of contamination typically arises from the rupture of underground storage tanks, application of pesticides, percolation of contaminated surface water to subsurface strata, oil and fuel dumping, leaching of wastes from landfills or direct discharge of industrial wastes to the soil. The most common chemicals involved are petroleum hydrocarbons, solvents, pesticides, lead and other heavy metals. An estimated 12 million tonnes of grain are contaminated by heavy metals every year, causing direct losses of 20 billion yuan (US\$2.57 billion).¹⁶ The United States, while having some of the most widespread soil contamination, has actually been a leader in defining and implementing standards for cleanup.¹⁷ Other industrialized countries have a large number of contaminated sites, but lag the U.S. in executing remediation. Developing countries may be leading in the next generation of new soil contamination cases. Each year in the U.S., thousands of sites complete soil contamination cleanup, some by using microbes that “eat up” toxic chemicals in soil¹⁸, many others by simple excavation and others by more expensive high-tech soil vapor extraction or air stripping. Efforts proceed worldwide to identify new sites of soil contamination.

Health effects

The major concern is that there are many sensitive land uses where people are in direct contact with soils such as residences, parks, schools and playgrounds. Other contact mechanisms include

contamination of drinking water or inhalation of soil contaminants which have vaporized. There is a very large set of health consequences from exposure to soil contamination depending on pollutant type, pathway of attack and vulnerability of the exposed population. Chromium and many of the pesticide and herbicide formulations are carcinogenic to all populations. Lead is especially hazardous to young children, in which group there is a high risk of developmental damage to the brain and nervous system, while to all populations kidney damage is a risk. Chronic exposure to benzene at sufficient concentrations is known to be associated with higher incidence of leukemia. Mercury and cyclodienes are known to induce higher incidences of kidney damage, some irreversible. PCBs and cyclodienes are linked to liver toxicity. Organophosphates and carbamates can induce a chain of responses leading to neuromuscular blockage. Many chlorinated solvents induce liver changes, kidney changes and depression of the central nervous system. There is an entire spectrum of further health effects such as headache, nausea, fatigue, eye irritation and skin rash for the above cited and other chemicals. At sufficient dosages a large number of soil contaminants cause death.

Ecosystem effects

Not unexpectedly, soil contaminants can have significant deleterious consequences for ecosystems.¹⁹ There are radical soil chemistry changes which can arise from the presence of many hazardous chemicals even at low concentration of the contaminant species. These changes can manifest in the alteration of metabolism of endemic microorganisms and arthropods resident in a given soil environment. Contaminants typically alter plant metabolism, most commonly to reduce crop yields.

Regulatory framework

United States of America

Until about 1970 there was little widespread awareness of the worldwide scope of soil contamination or its health risks. In fact, areas of concern were often viewed as unusual or isolated incidents. Since then, the U.S. has established guidelines for handling hazardous waste and the cleanup of soil pollution. In 1980 the U.S. Superfund/CERCLA established strict rules on legal liability for soil contamination. Not only did CERCLA stimulate identification and cleanup of thousands of sites, but it raised awareness of property buyers and sellers to make soil pollution a focal issue of land use and management practices. While estimates of remaining soil cleanup in the U.S. may exceed 200,000 sites, hundreds of new sites are identified each year, and in other industrialized countries there is a lag of identification and cleanup functions. Even though their use of chemicals is lower than industrialized countries, often their controls and regulatory framework is quite weak.

United Kingdom

Generic guidance commonly used in the UK are the Soil Guideline Values published by DEFRA and the Environment Agency. These are screening values that demonstrate the minimal acceptable level of a substance. Above this there can be no assurances in terms of significant risk of harm to human health. These have been derived using the Contaminated Land Exposure Assessment Model (CLEA UK). Certain input parameters such as Health Criteria Values, age and land use are fed into CLEA UK to obtain a probabilistic output. Guidance by the Inter Departmental Committee for the Redevelopment of Contaminated Land (ICRCL) has been formally withdrawn by the Department for Environment, Food and Rural Affairs (DEFRA), for

use as a prescriptive document to determine the potential need for remediation or further assessment. Therefore, no further reference is made to these former guideline values. Other generic guidance that exists (to put the concentration of a particular contaminant in context), includes the United States EPA Region 9 Preliminary Remediation Goals (US PRGs), the US EPA Region 3 Risk Based Concentrations (US EPA RBCs) and National Environment Protection Council of Australia Guideline on Investigation Levels in Soil and Groundwater. However international guidance should only be used in the UK with clear justification. Three sets of CLEA SGVs have been produced for three different land uses, namely residential (with and without plant uptake) allotments commercial/industrial. It is intended that the SGVs replace the former ICRL values. It should be noted that the CLEA SGVs relate to assessing chronic (long term) risks to human health and do not apply to the protection of ground workers during construction, or other potential receptors such as groundwater, buildings, plants or other ecosystems. The CLEA SGVs are not directly applicable to a site completely covered in hardstanding, as there is no direct exposure route to contaminated soils.

Cleanup options



Microbes can be used in soil cleanup

Cleanup or remediation is analyzed by environmental scientists who utilize field measurement of soil chemicals and also apply computer models for analyzing transport¹⁹ and fate of soil chemicals. Thousands of soil contamination cases are currently in active cleanup across the U.S. as of 2006. There are several principal strategies for remediation:

Excavate soil and take it to a disposal site away from ready pathways for human or sensitive ecosystem contact. This technique also applies to dredging of bay muds containing toxins.

Aeration of soils at the contaminated site (with attendant risk of creating air pollution)

Thermal remediation by introduction of heat to raise subsurface temperatures sufficiently high to volatilize chemical contaminants out of the soil for vapour extraction. Technologies include ISTD, electrical resistance heating (ERH), and ET-DSPtm.

Soil pH

Soil pH is a measure of the soil acidity or Soil alkalinity. An acid solution has a pH value less than 7. While a basic solution always has a pH larger than 7, an alkaline solution (i.e. a solution with positive acid neutralizing capacity) does not necessarily have a pH larger than 7. For details on the relation between pH and ANC, see acid neutralizing capacity. Soil pH is an important consideration for farmers and gardeners for several reasons: Many plants and soil life forms prefer either alkaline or acidic conditions. Some diseases tend to thrive when the soil is alkaline or acidic. The pH can affect the availability of nutrients in the soil.

Nutrient availability in relation to soil pH

The majority of food crops prefer a neutral or slightly acidic soil (pH 7). Some plants however prefer more acidic (e.g., potatoes, strawberries) or alkaline (brassicas) conditions. Once the cation exchange surface has become depleted of these ions, however, the concentration in soil solution can be quite low and is largely determined by the weathering rate. The weathering rate in turn is dependent on such things as mineralogy (e.g. presence of easily weathered minerals), surface area (i.e. the soil texture), soil moisture (i.e. how large a fraction of the mineral surface area that is wet), pH, concentration of base cations such as Ca, Mg and K as well as concentration of aluminium. Naturally, taking a sample introduces a disturbance of the system, which can e.g. result in a change in nutrient uptake and decomposition rates (e.g. due to cutting of fine roots when placing the lysimeter). Many nutrient cations such as zinc (Zn^{2+}), aluminium (Al^{3+}), iron (Fe^{2+}), copper (Cu^{2+}), cobalt (Co^{2+}), and manganese (Mn^{2+}) are soluble and available for uptake by plants below pH 5.0, although their availability can be excessive and thus toxic in more acidic conditions. In more alkaline conditions they are less available, and symptoms of nutrient deficiency may result, including thin plant stems, yellowing (chlorosis) or mottling of leaves, and slow or stunted growth. pH levels also affect the complex interactions among soil chemicals. Phosphorus (P) for example requires a pH between 6.0 and 7.5 and becomes chemically immobile outside this range, forming insoluble compounds with iron (Fe) and aluminium (Al) in acid soils and with calcium (Ca) in calcareous soils.

Soils and acidity

Under conditions in which rainfall exceeds evapotranspiration (leaching) during most of the year, the basic soil cations (Ca, Mg, K) are gradually depleted and replaced with cations held in colloidal soil reserves, leading to soil acidity. In addition, the following nitrate fertilizers -- calcium nitrate, magnesium nitrate, potassium nitrate and sodium nitrate -- also increase the soil pH value. Some alkaline soils have calcium in the form of limestone that is not chemically available to plants. In this case sulfuric acid

Factors affecting soil pH

The pH value of a soil is influenced by the kinds of parent materials from which the soil was formed. Soils developed from basic rocks generally have higher pH values than those formed from acid rocks. Rainfall also affects soil pH. Water passing through the soil leaches basic nutrients such as calcium and magnesium from the soil. They are replaced by acidic elements such as aluminium and iron. For this reason, soils formed under high rainfall conditions are more acidic than those formed under arid (dry) conditions.

Soil life and pH

A pH level of around 6.3-6.8 is also the optimum range preferred by most soil bacteria, although fungi, molds, and anaerobic bacteria have a broader tolerance and tend to multiply at lower pH values. Therefore, more acidic soils tend to be susceptible to souring and putrefaction, rather than undergoing the sweet decay processes associated with the decay of organic matter, which immeasurably benefit the soil. These processes also prefer near-neutral conditions.

pH and plant diseases

Many plant diseases are caused or exacerbated by extremes of pH, sometimes because this makes essential nutrients unavailable to crops or because the soil itself is unhealthy (see above). For example, chlorosis of leaf vegetables and potato scab occur in overly alkaline conditions, and acidic soils can cause clubroot in brassicas.

Determining pH

The pH should be measured regularly and at various points within the land in question. Methods of determining pH include:

Observation of soil profile. Strongly acidic soils often have poor incorporation of the organic surface layer with the underlying mineral layer. The mineral horizons are distinctively layered in many cases, with a pale eluvial (E) horizon beneath the organic surface; this E is underlain by a darker B horizon in a classic podzol horizon sequence. This is a very rough gauge of acidity as there is no correlation between thickness of the E and soil pH. E horizons a few feet thick in Florida usually have pH just above 5 (merely "strongly acid") while E horizons a few inches thick in New England are "extremely acid" with pH readings of 4.5 or below.[1][2] [3]In the southern Blue Ridge Mountains there are "ultra acid" soils, pH below 3.5, which have no E horizon.[4] Observation of predominant flora. Calcifuge plants (those that prefer an acidic soil) include Erica, Rhododendron and nearly all other Ericaceae species, many Betula (birch), Digitalis (foxgloves), gorse, and Scots Pine. Calcicole (lime loving) plants include Fraxinus (Ash), Honeysuckle (Lonicera), Buddleia, Cornus spp (dogwoods), Lilac(Syringa) and Clematis spp. Observation of symptoms that might indicate acidic or alkaline conditions, such as occurrence of the plant diseases mentioned above or salinisation of alkaline soils. The house hydrangea (*Hydrangea macrophylla*) produces pink flowers at pH values of 6.8 or higher, and blue flowers at pH 6.0 or below. Use of an inexpensive pH testing kit based on barium sulfate in powdered form, where in a small sample of soil is mixed with water which changes colour according to the acidity/alkalinity. Use of litmus paper. A small sample of soil is mixed with distilled water, into which a strip of litmus paper is inserted. If the soil is acidic the paper turns red, if alkaline, blue. Use of a commercially available electronic pH meter, in which a rod is inserted into moistened soil and measures the concentration of hydrogen ions.

Increasing soil pH

The aim when attempting to adjust soil acidity is not so much to neutralise the pH as to replace lost cation nutrients, particularly calcium. This can be achieved by adding limestone to the soil, which is available in various forms: Agricultural lime (ground limestone or chalk) is used for soil liming. These natural forms of calcium carbonate are probably the cheapest form of lime for gardening and agricultural use and can be applied at any time of the year. These forms are slow reacting, thus their effect on soil fertility and plant growth is steady and long lasting. Ground lime should be applied to clay and heavy soils at a rate of about 500 to 1,000 g/m² (1 to 2 lb/yd² or 4,500 to 9,000 lb/ac). The concept of "corrected lime potential"²⁰ to define the degree of base saturation in soils became the basis for procedures now used in soil testing laboratories to determine the "lime requirement" of soils.²⁰ Quicklime and slaked lime: The former is produced by burning rock limestone in kilns. It is highly caustic and cannot be applied directly to the soil. Quicklime reacts with water to produce slaked, or hydrated, lime, thus quicklime is spread around agricultural land in heaps to absorb rain and atmospheric moisture and form slaked lime, which is then spread on the soil. Quicklime should be applied to heavy clays at a rate of about 400 to 500 g/m² (0.75 to 1 lb/yd² or 3,600 to 4,500 lb/ac), hydrated lime at 250 to 500 g/m² (0.5 to 1 lb/yd²). However, quicklime and hydrated lime are very fast acting and are not suitable for inclusion in an organic system. Calcium sulfate (gypsum) cannot be used to amend soil acidity. It is a common myth that gypsum affects soil acidity.²⁰ However, gypsum does reduce aluminium toxicity. Because gypsum is more soluble than alkaline earth carbonates, it is recommended for the treatment of acidic subsoils.²⁰

Reducing soil pH

The pH of an alkaline soil is lowered by adding sulfur, iron sulfates or aluminium sulfate, although these tend to be expensive, and the effects short term.

Urea, urea phosphate, ammonium nitrate, ammonium phosphates, ammonium sulfate and monopotassium phosphate also lower soil pH. Fertilizers often also affect a slightly more acidic soil since this increases uptake of nutrients. Decayed vegetable matter, compost, stable manure, urea, etc.

Sulfur cycle

Sulfur is one of the constituents of many proteins, vitamins and hormones. It recycles as in other biogeochemical cycles. The essential steps of the **sulfur cycle** are: Mineralization of organic sulfur to the inorganic form, hydrogen sulfide: (H_2S). Oxidation of sulfide and elemental sulfur (S) and related compounds to sulfate (SO_4^{2-}). Reduction of sulfate to sulfide. Microbial immobilization of the sulfur compounds and subsequent incorporation into the organic form of sulfur. These are often termed as follows: Assimilative sulfate reduction (see also sulfur assimilation) in which sulfate (SO_4^{2-}) is reduced to organic sulfhydryl (otherwise known as thiol) groups (R-SH) by plants, fungi and various prokaryotes. The oxidation states of sulfur are +6 in sulfate and -2 in R-SH. Desulfuration in which organic molecules containing sulfur can be desulfurated, producing hydrogen sulfide gas (H_2S), oxidation state = -2. Note the similarity to deamination. Oxidation of hydrogen sulfide produces elemental sulfur (S^0), oxidation state = 0. This reaction is done by the photosynthetic green and purple sulfur bacteria and some chemolithotrophs. Further oxidation of elemental sulfur by sulfur oxidizers produces sulfate. Dissimilative sulfur reduction in which elemental sulfur can be reduced to hydrogen sulfide. Dissimilative sulfate reduction in which sulfate reducers generate hydrogen sulfide from sulfate.

Conclusion

The present review emphasize on the current scenario of the soil chemistry and pollution control requires to overcome the problems associated with it. The present needs of increasing the productivity of the soil to fulfill the need of food is best achieved by practicing the chemical characterization of the soil at a regular interval. It also provides the overview of various characterization methods and tools used in soil chemistry. It will help out those who are related to the field.

Referernces

1. Sonon, L. S. , M. A. Chappell and V.P. Evangelou; *The History of Soil Chemistry*; 2000.
2. D. Dent,. *Acid sulphate soils: a baseline for research and development*. Publ. 39, ILRI, Wageningen, The Netherlands. 1986.
3. *Rice Polders Reclamation Project, Guinea Bissau*. International Institute for Land Reclamation and Improvement (ILRI), Wageningen, The Netherlands. In: *Annual Report 1980*, 26–32.
4. *Agricultural Land Drainage: A wider application through caution and restraint*. International Institute for Land Reclamation and Improvement (ILRI), Wageningen, The Netherlands. In: *Annual Report 1991*, p.21–35.

5. H.S. Sen and R.J. Oosterbaan, Research on Water Management and Control in the Sunderbans, India. International Institute for Land Reclamation and Improvement (ILRI), Wageningen, The Netherlands. In: Annual Report 1992, p. 8-26.
6. Review of water management aspects in Pulau Petak (near the town of Bandjermasin, Kalimantan, Indonesia). Mission Report 39, Research Project on Acid Sulphate (Sulfate) Soils in the Humid Tropics. International Institute of Land Reclamation and Improvement (ILRI), Wageningen, The Netherlands.
7. R.Brinkman, Saline and sodic soils. In: Land Reclamation and Water Management, ILRI publication 27, 1988;p.62-68.
8. G.H.Bolt (ed.), Soil chemistry: A. basic elements. Vol 5a, Elsevier, Amsterdam, The Netherlands; 1981.
9. Chhabra, R. Soil Salinity and Water Quality. Oxford&IBH Publishing Co. Pvt. Ltd., New Delhi (South Asian edition) and A.A. Balkema Uitgevers BC, Rotterdam ; 1996; pp 284.
10. Sedjo, Roger.. The Carbon Cycle and Global Forest Ecosystem. Water, Air, and Soil Pollution 70, 1993;295-307. Trends in Carbon Dioxide — NOAA Earth System Research Laboratory
11. Monterey Bay Aquarium Research Institute (MBARI) (2005-06-09). ""Sinkers" provide missing piece in deep-sea puzzle". Press release. http://www.mbari.org/news/news_releases/2005/sinkers-release.pdf. Retrieved 2007-10-07.
12. Typhoons Bury Tons of Carbon in the Oceans Newswise, Retrieved on July 27, 2008.
13. Millero, Frank J.. Chemical Oceanography (3 ed.). CRC Press. 2005.
14. Risk Assessment Guidance for Superfund, Human Health Evaluation Manual, Office of Emergency and Remedial Response, U.S. Environmental Protection Agency, Washington D.C. 20450
15. Rainer Stegmann, Treatment of Contaminated Soil: Fundamentals, Analysis, Applications, Springer Verlag, Berlin 2001.
16. D.A. Crossley, Roles of Microflora and fauna in soil systems, International Symposium on Pesticides in Soils, Feb. 25, 1970.
17. Michael Hogan, Leda Patmore, Gary Latshaw and Harry Seidman Computer modeling of pesticide transport in soil for five instrumented watersheds, prepared for the U.S. Environmental Protection Agency Southeast Water laboratory, Athens, Ga. by ESL Inc., Sunnyvale, California ;1973.
18. S.K. Gupta, C.T. Kincaid, P.R. Mayer, C.A. Newbill and C.R. Cole, ‘‘A multidimensional finite element code for the analysis of coupled fluid, energy and solute transport’’, Battelle Pacific Northwest Laboratory PNL-2939, EPA contract 68-03-3116 1982 .
19. One Hundred Harvests Research Branch Agriculture Canada 1886-1986". Historical series / Agriculture Canada - Série historique / Agriculture Canada. Government of Canada. Retrieved 2008-12-22.
20. Smith, C. J.; Peoples, M. B. Keerthisinghe, G. James, T. R.. "Effect of surface applications of lime, gypsum and phosphogypsum on the alleviating of surface and subsurface acidity in a soil under pasture". Australian Journal of Soil Research **32** (5):1994;995–1008.