

CHAPTER 2

GEOCHEMISTRY OF THE TROPICAL ENVIRONMENT

TROPICAL ENVIRONMENT

Tropical regions cover approximately 40% of the surface of the earth and have a diversity of climates. As noted by Köppen (1936), two broad categories of tropical climates can be distinguished, namely tropical rainforest and periodically dry savannah. Depending on the rainfall, these two categories are often further subdivided.

The Food and Agricultural Organization (FAO, 1978) proposed a more detailed climatic characterization defining agro-ecological zones for the developing world. Subsequently, the FAO (1993) simplified and broadened the agro-ecological zoning method to illustrate the distribution of the major soil resources globally (Fig. 2.1). In the context of the tropical environment, only four subdivisions were considered relevant:

- (a) Arid zone.
- (b) Seasonally dry tropics and sub-tropics.
- (c) Humid tropics and sub-tropics, and
- (d) Mountainous zone.

From the point of view of medical geology, an agriculture-based classification becomes useful on account of the rock-soil-water-plant-human relationships.

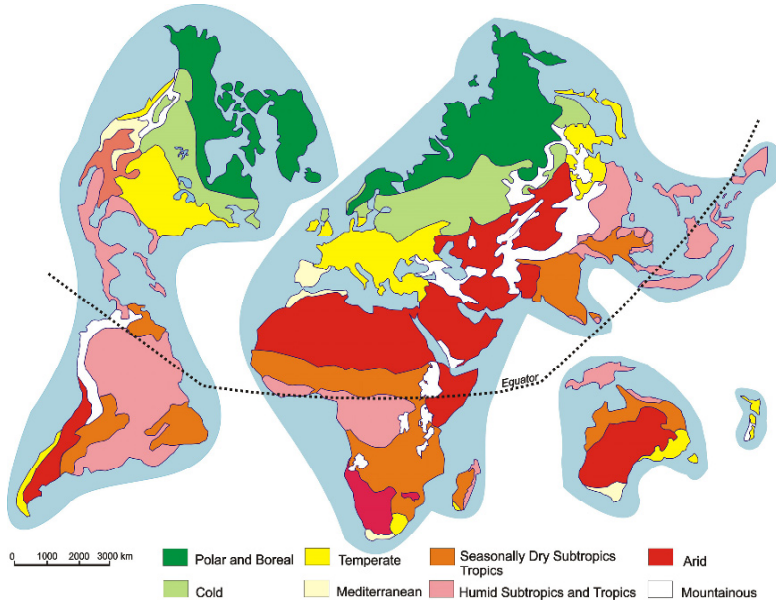


Fig. 2.1. World's major climates (FAO, 1978)

Subdivisions of the Tropical Environment

Arid zone

The arid climatic zone is characterized by an length of growing periods (LGP) of less than 75 days. The major arid areas include the Sahara, the Kalahari, the Namibian desert and the Horn of Africa. Other areas include the Arabian Peninsula, Central Asia, the western United States, the North Western parts of Brazil, South Western part of Latin America and Central Australia.

Due to the very short LGP, agricultural crops cannot complete their normal cycle and yields, if any, are insignificant. Further, the non-availability of soil moisture for most of the year, results in soil characterisation being affected. Weathering is therefore extremely slow. From among the pedogenetic processes, migration and accumulation of soluble salts, calcium carbonate and gypsum are perhaps the only functional processes and these result in Solonchaks and Solonetz, Calcisols and Gypsisols. The extremely strong wind action causes the formation of sandy soils (Arenosols) which

have a lack of finer particles. Soil horizon development is virtually non-existent under these climatic conditions.

Seasonally dry tropics and sub-tropics

This type of climate is observed in the tropics and sub-tropics where the dry season prevails between 90 to 285 days and the rainfall is not confined to the winter. As shown in Fig 2.1, this zone covers approximately 2475 million ha and includes large areas of South and Southeast Asia, Northern Australia, the major part of Africa, South and Central America between the deserts and the tropical rain forests.

As observed by the FAO (1993), the climate dependent agriculture potential of this zone is heavily determined by the length and intensity of the dry season. The relatively high temperatures prevailing in the zone and the pronounced wet season favours rock weathering and soil formation with the accumulation of silica and alumina resulting in clay formation, mostly kaolinite. As shown in Table 2.1 and 2.2, Ferralsols, Acrisols and Lixisols are more abundant in this zone. When the parent rocks are abundant in Ca and Mg, smectites form and this gives rise to Vertisols.

Humid tropics and sub-tropics

This climatic zone which covers approximately 1925 millions ha, is characterized by high temperatures throughout the year and alternating wet and dry seasons. Areas such as central and coastal West Africa, the Amazon Basin, Southeast Asia and the islands of the Pacific Ocean belong to this climatic zone. The combined hot and wet climatic features of the zone provide ideal conditions for the growth of tropical rain forests and also agricultural productivity for most of the year.

Weathering is intense and the soil profile often reaches depths of as much as 150 m. Kaolinitic clays are very common and on account of the intense rainfall, nutrients are easily leached out. Among the soils present are Ferralsols (extremely weathered soils), Acrisols (less weathered) and these cover about 57% of the land of the climatic zone (Table 2.1). Groundwater tends to be abundant and this results in the formation of Gleysols and Pod-sols.

Table 2.1. Extent (units of 1000 ha) of major soil groups by climatic zone in the tropics and subtropics (FAO, 1993)

	Arid	Mountainous	Seasonally dry tropics and Sub- tropics	Humid Trop- ics and Sub- tropics
Histosols	3410	792	12232	32449
Leptosols	419462	544330	198332	66731
Vertisols	51243	3820	222983	29012
Fluvisols	90074	4401	84360	66207
Solonchaks	140324	3608	20824	4415
Gleysols	34492	11002	111543	167704
Andosols	9418	20683	18379	20674
Arenosols	395942	6980	320140	127284
Regosols	170083	35916	52109	9391
Podzols	1366	3221	13475	11343
Plinthisols	53	255	15657	42354
Ferralsols	0	4036	231347	507217
Planosols	3762	2609	74083	6267
Solonetz	57037	5367	36771	518
Greyzems	2230	5010	0	0
Chernozems	11794	1802	0	0
Kastanozems	143513	17569	44729	459
Phaeozems	2089	8721	15249	2703
Podzoluvisols	0	17358	0	0
Gypsisols	86711	1666	54	0
Calcisols	552765	44857	47267	5430
Nitisols	2792	9996	101782	87291
Acrisols	1067	13581	238808	589386
Luvisols	165499	13541	62002	21827
Lixisols	26397	11390	366862	31697
Cambisols	503586	153299	192294	95617
TOTAL	2875109	945810	2481282	1925976

Mountainous zone

The sudden changes in altitude and varying morphology of the slopes bring about marked climatic changes. The temperature and rainfall therefore change quite significantly over short distances. There is great heterogeneity in vegetation and some of the lands are of the fragile type. From the foregoing account, it is clear that the climate is perhaps the most critical determinant of the agricultural productivity, influencing the soil formation and nutrient availability.

Table 2.2. Extent (units of 1000s ha) of main soil groups by continent (FAO, 1993)

	Europe	North & C. Asia	Australasia	North America
Leptosols	64836	710863	48789	83303
Cambisols	157288	452241	81084	169019
Acrisols	4170	148241	32482	114813
Arenosols	3806	3436	193233	25512
Calcisols	56657	95264	113905	114720
Ferralsols	0	0	0	0
Gleysols	17641	323611	421	131053
Luvissols	142658	99739	127445	179244
Regosols	26848	33169	887	283933
Podzols	213624	21825	8459	220770
Kastanozems	55598	173265	1827	153704
Lixisols	0	0	0	0
Fluvisols	40250	73327	8827	10387
Vertisols	5856	11797	90019	9120
Podzoluvisols	161684	153911	0	5470
Histosols	32824	99451	1167	934562
Chernozems	98551	90566	0	40101
Nitisols	0	0	10100	0
Solonchaks	2308	46895	16565	127
Phaeozems	9221	19948	3562	70320
Solonetz	7906	30062	38099	10748
Planosols	1877	2413	38941	6500
Andosols	4058	18361	6953	17590
Gypsisols	379	16494	0	0
Plinthosols	0	0	3895	2816
Greyzems	6090	23331	0	4462
	Africa	South & SE Asia	South & C. America	Total
Leptosols	381531	119408	246588	1655318
Cambisols	369232	209385	135153	1573402
Acrisols	92728	263005	341161	996600
Arenosols	462401	94530	118967	901885
Calcisols	171237	220068	24318	796169
Ferralsols	319247	0	423353	742600
Gleysols	122313	37084	86707	718830
Luvissols	17609	41332	40478	648505
Regosols	140684	64357	29093	578971
Podzols	11331	5982	5522	487513
Kastanozems	2802	0	80561	467757
Lixisols	244830	86145	105545	436520
Fluvisols	98400	57357	67687	356235

Vertisols	106126	76328	38076	337322
Podzoluvisols	0	0	0	321065
Histosols	12270	24829	9245	273248
Chernozems	0	0	0	229218
Nitisols	98510	48796	48112	205518
Solonchaks	48574	48512	24344	187325
Phaeozems	341	1855	48992	154239
Solonetz	13800	0	34652	135267
Planosols	18944	4655	56566	129896
Andosols	5270	8840	45973	107045
Gypsisols	51757	21387	0	90017
Plinthosols	7992	1711	44721	61135
Greyzems	0	0	0	33883

ROCK WEATHERING AND SOIL FORMATION IN THE TROPICS

As discussed in the earlier section, the tropical environment is characterized by seasonal heavy rainfall (exceeds 5000 mm per year in some cases), with long periods of drought and high ambient temperatures. The intensity of chemical weathering is therefore extreme and some of the tropical soils are weathered to such an extent (Fig 2.2), that potassium, an essential plant nutrient usually present in appreciable concentrations is present only in trace amounts (Fyfe et al., 1983). Coincidentally, the world's most underdeveloped countries also lie in such tropical environments where poor agricultural productivity caused by the impoverishment of soil in essential nutrients has had a marked impact on the economy of these countries over the years.

Fyfe et al. (1983) noted that soils in such regions will be dominated by minerals such as gibbsite, goethite, kaolinite and quartz. A few trace elements are expected to remain in refractory minerals such as zircon, rutile etc, but the critically important feature is that most bio-essential elements are reduced to extremely low levels. These soils were termed "impossible soils".

In another interesting study on the chemistry of some Brazilian soils, where chemical leaching of elements was extreme, Kronberg et al. (1979) observed that trace elements show a wide range of behaviour and that the major elements had severely leached. They showed that the trace element behaviour appears to be largely controlled by the dominant clay or Al_2O_3 -

SiO_2 minerals or the degree of weathering. The main components (SiO_2 - Al_2O_3 - Fe_2O_3 - H_2O) are known to be present mineralogically as quartz, kaolinite, goethite and hematite.

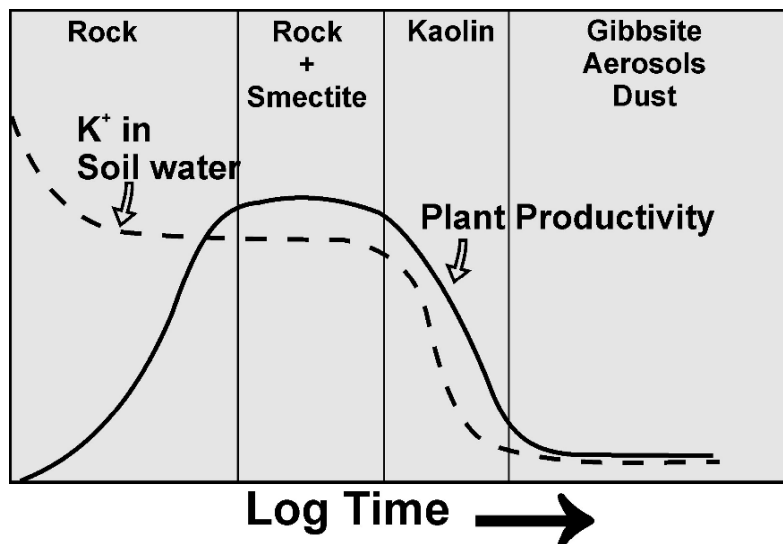


Fig. 2.2. A schematic diagram showing weathering progress from rock to bauxite and plant productivity (Fyfe et al., 1983)

Some of the tropical environments are characterized by very thick laterite profiles over 150 m thick (Fig 2.3) and it has been established that it has taken tens of millions of years for these thick laterite profiles to form. With respect to crustal abundance, except for the least soluble refractory oxides of elements such as Sc, Zr, Nb, Gd, Tm and Th and some bio-important elements such as B, Cl, Mo, Se, Sn and I, most other elements are highly depleted. Figure 2.4 illustrates the relationship of geochemistry and the kinetics of plant nutrition. Such a relationship will undoubtedly have an important bearing on the medical geochemistry of that particular environment.

The clays which form from unweathered rocks are of three types namely smectites, illites and kaolin in order of decreasing complexity. In the presence of smectite clays in association with unweathered minerals, many trace elements such as Zn, Cu, Rb, Cs, tend to get concentrated in the weathering process. According to Fyfe et al. (1983), when the primary minerals are leached and their surface areas are reduced to the point where solution concentrations drop below their metastable solubilities, the smectite

and other complex clays begin to degrade with kaolin increasing in abundance in the soil. Humid tropical environments are the best locations for such processes.



Fig. 2.3. A thick laterite profile from Sri Lanka

As shown in Figure 2.4, if K_2 exceeds K_1 , there will be depletion of essential elements and if K_1 ceases to operate, the levels of most essential nutrients (major and trace) will fall below the optimum value for nutrition and as a result of this infertility prevails. When the essentiality of trace elements in human and animal health are taken into consideration, an understanding of such a rock-soil-plant relationship in a terrain becomes all the more important.

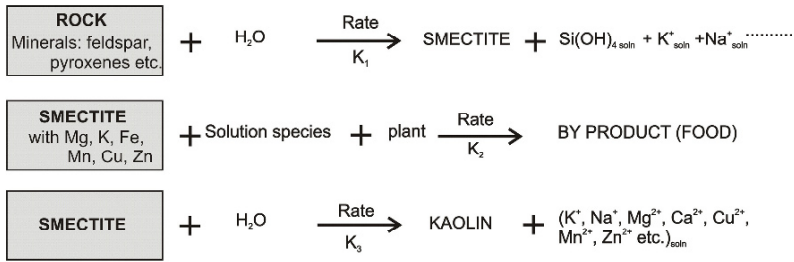


Fig. 2.4. Geochemistry and the kinetics of nutrition (Fyfe et al., 1983)

The generalized relationships between regolith, thickness of the weathering zone, climatic factors and water chemistry are shown in Figure 2.5. It has also been observed that the organic matter in the soil also tends to get depleted due to intense oxidation which often extends to the weathering front. This is generally accompanied by the depletion of some major elements such as P, N and K and soluble cations such as Na^+ and Ca^{2+} as well as anions Cl^- , PO_4^{3-} and NO_3^- . The natural vegetation of these infertile soils is therefore low and the essential trace elements needed for human and animal health become relatively sparse.

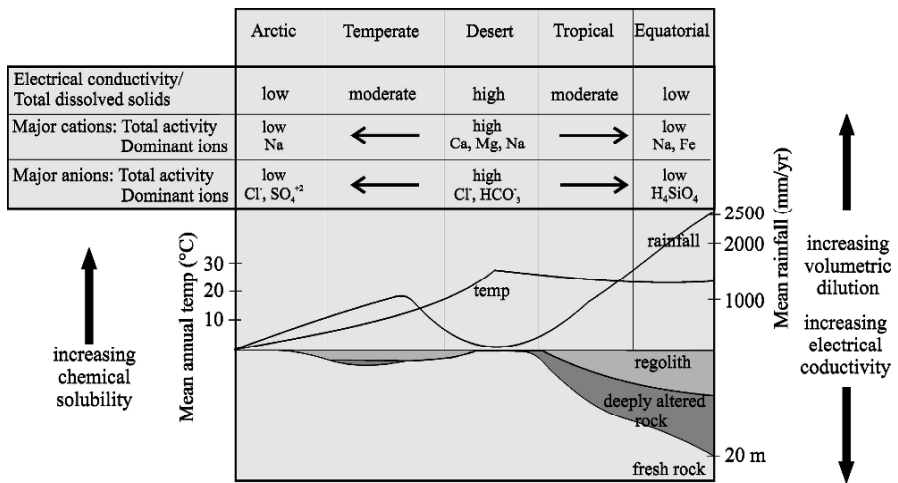


Fig. 2.5. Generalized relationships between regolith, thickness of weathering zone, climatic factors and water chemistry (Plant et al., 1996; Pedro, 1985)

Under tropical environmental conditions, element fractionation in the weathering of rocks and soil formation result in heterogeneous distribution of elements in terrains. Accordingly, areas of unique geochemical features develop with their inherent deficiency or excess of trace and major elements.

These special areas could also be termed as “geochemical provinces” and as shown in later chapters, they form an important facet of medical geology of tropical environments.

The bioavailability of essential and toxic elements plays a major role in the aetiology of environment-related diseases and this is influenced to a marked degree by the mobility or non-mobility of the elements concerned in the “rock-soil” environment. The laterites, so typical of the tropical environment, often function as “scavengers” of cations and anions and these, therefore, control the distribution of the elements in the ‘geochemical provinces’ to a marked degree. There are numerous external and internal factors that are responsible for the concentration and partitioning of elements in laterites.

The presence of active surfaces on which element adsorption and concentration takes place is an essential pre-requisite. Laterites contain abundant amorphous and poor crystalline constituents that show high adsorption rates. These were termed “scavengers” by Kühnel (1987).

The following are considered as common “scavengers” in soils and laterites, (i) amorphous silica (ii) Fe, Al and Mn-oxyhydroxides (iii) organic matter. Clay minerals such as smectite as well as phosphates, carbonates and some sulphides are also known to act as “scavengers”. The high ability of these mineral phases to take up and fix elements from migrating solutions is mostly due to the presence of a very large surface area, which enhances chemical reactivity to a marked degree. The minute particle size and the amorphous nature is particularly responsible for the presence of the large surface area.

The ability of the “scavengers” to trap all available particles including water molecules, cations, or anions is governed by the need to compensate for the charge imbalances in the amorphous surface. Table 2.3 shows examples of some “scavengers” in laterites and soils present in the tropical environment.

Table 2.3. Examples of some “scavengers” in laterites and soils (Kühnel, 1987)

Scavenger	Collected cations (anions)	Possible products after recrystallization
Fe-oxyhydroxides	Ti, Cr, Al	magnetite, maghemite, hematite
	Cr, Al, Ni, Co, (F) Co Cu (AsO ₄)	goethite and other FeOOH poly- morphs goethite + heterogenite delafossite, goethite + cuprite goethite + struvite
Mn-oxyhydroxides	Co, Ni	
	Ba, Zn, Al	todorokite, woodruffite
	Li, Al	psilomelane
	K, Na	lithiophorite
	Zn, Pb, Ag	cryptomelane, birnessite
	Ca, Mg	hetaerolite, quenselite
Silica	Fe, Mg (SiO ₄)	marokite bixbyite, jacobsite braunite
	Al, Ni, Na, K	
Al-oxyhydroxides +silica +magnesia	Cu	opal, jasper, quartz chryocolla
	Ni, Co, Cr	
	Ni	clay minerals
	Cu	smectites
	Ni, Fe, Al	talc, sepiolite, serpentinite
	Ni(CO) ₃ , (SO ₄)	vermiculite pyroaurite pyroaurite, takovite

Tropical Weathering of Mineralized Terrains

Intense weathering in mineralized terrains in tropical environments brings about unique changes in the geochemistry and mineralogy in the terrain. People living in such areas are often subjected to a unique geochemistry. The largest reserves and resources of lateritic nickel for example, occur in developing countries in the tropics and sub-tropics.

The conditions necessary for the formation of laterite deposits resulting in the concentration of Ni, Co, Cr and Al are well known. Dissanayake (1984a) briefly discussed the main criteria for tropical weathering:

- (a) Climate: a humid tropical or sub-tropical climate with seasonal changes of rainfall and temperature promotes the laterization proc-

ess. Due to the high intensity of the rainfall, metals are easily brought into solution and leached away. During the dry season, saturation of the metal ions in solution is followed by precipitation at specific physico-chemical environments resulting in concentrations of metals at various levels.

- (b) **Drainage:** Good porosity of the rocks and easy drainage permit the circulation of leaching groundwaters. This enables the chemical processes involved in the weathering to achieve completion.
- (c) **Topography:** Regions with strongly pronounced relief are not conducive to weathering, since erosion outweighs chemical weathering. A flat or nearly flat topography, especially on old land surfaces, enables optimum water table conditions to operate with the resulting accumulation of the products of chemical weathering.
- (d) **Time:** Prolonged exposure to the above mentioned factors under stable tectonic conditions results in the near completion of the weathering processes and the presence of weathering products at different stages of evolution indicates the relative time of exposure.
- (e) **Parent rocks:** Ultrabasic rocks such as peridotites are known to contain significant contents of Ni, Co and Cr (Turekian and Wedepohl, 1961) and the availability of such rocks covering large areas is a necessary criterion for the concentration of Ni, Co and Cr in the laterites.

Weathering Profiles

In lateritic terrains, weathering of different stages of evolution can be seen. Alteration of ultrabasic rocks into laterite involves complicated processes resulting in extreme changes of physical, chemical and mineralogical composition. Figure 2.6 illustrates two weathering profiles over serpentinites from Sri Lanka and Indonesia, respectively, the latter showing the mineralogical composition.

Weathering of Nickeliferous Serpentinites

In a typical cross-section, a distinct transition from the uppermost weathering products to the unaltered primary ultramafic rock can be seen. As shown in Figure 2.6 the lateritic iron ore or the cap can be seen on the top.

In places where decayed plant material is absent, the duricrust can be seen as a solid brown cap-like covering composed mainly of secondary iron-oxides and hydroxides. Iron has been leached out and re-precipitated by solution activity. On a nickeliferous serpentinite in Sri Lanka, Dissanayake (1984a) observed that the duricrust is distributed as bare patches generally devoid of vegetation. The iron-bearing material generally takes the form of massive rounded reddish brown nodules of a concretionary nature. It is common to find the surface strewn with such iron-ore concretions of varying sizes.

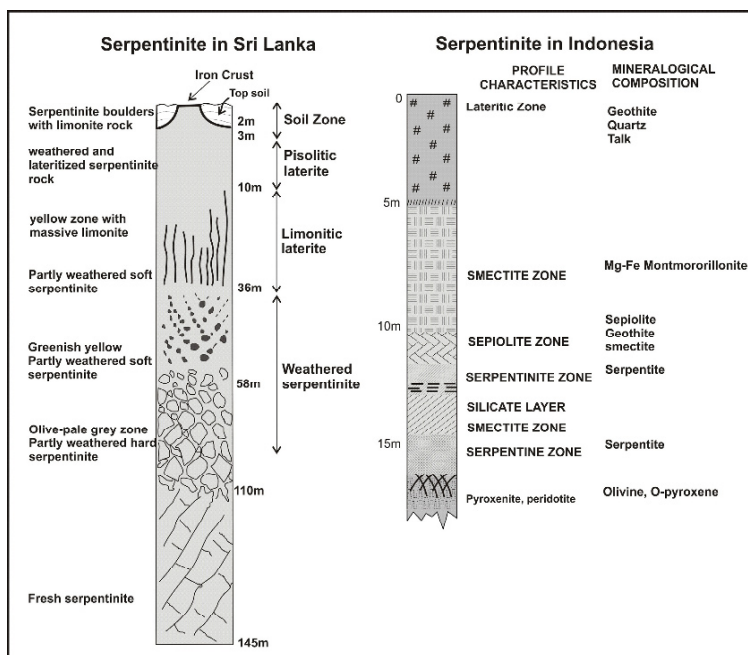


Fig. 2.6. Weathering profiles over serpentinite in Sri Lanka (Dissanayake, 1984a) and Indonesia (Kühnel et al., 1978)

Below the lateritic cap could be seen the remnants of highly weathered serpentinitized ultramafic rock retaining in most cases the original reticulate or banded structure. A conspicuous feature in this zone is the occurrence of small black grains of magnetite and chrome spinels. This feature has been observed in a number of case histories (Sri Lanka: Dissanayake and Van Riel, 1976; India: Ziauddin and Roy, 1970; Thailand: Pungrassami, 1970; Cuba: Fisher and Dressel, 1959). It is also common to find the weathered ultrabasic rock assuming varying shades of green. It is of interest to note that Brindley and Hang (1973) had observed a close correlation of the

intensity of green colour as determined by the Munsell colour chart, with the nickel content. This feature is worthy of consideration in nickel prospecting. Generally, the fragments and blocks become larger and more abundant downwards. The concentration of chrome-spinels, which are resistant to weathering increase upwards in the weathered zone. It is the material of this zone which needs to be analyzed carefully for nickel.

The next layer below is generally characterized by the occurrence of green coloured clays-sometimes called nontronites. While the original reticulate and banded structure may remain, the chrome-spinels and magnetite may be inconspicuous in this zone. Another important feature is the occasional occurrence of secondary silica in the form of chert, agate, opal and chalcedony. These have resulted from the leaching of silica by descending solutions and in the presence of significant concentrations of nickel assume a green colour.

Just above the fresh parent ultramafic rock is the partly weathered material. A noteworthy feature of this zone is the occurrence of carbonates in the form of calcite/magnesite. Their presence imparts a white appearance to the rock and pockets of shining white carbonate aggregates may indeed be found as in the case of the nickeliferous serpentinite of Sri Lanka.

The above-mentioned weathering profile, even though highly generalized, can be observed over ultramafic rocks in humid tropical terrains. The thickness of the various zones, however, varies widely depending on the locations. In some instances as in the case of the Moa serpentinitized ultramafic mass of Cuba (Linchenat and Shirokova, 1964), the weathering profile may attain depths greater than 50 metres. It should be noted that nickel is concentrated in the weathered serpentinite zone up to about 10 times the parent rock value and generally reaches a peak close to the upper boundary zone. This feature of nickel being concentrated at the base of the weathering profile is very characteristic of most nickeliferous laterites and should be noted carefully. It is also of interest to note that cobalt is concentrated slightly above the zone where nickel is enriched.

Formation of Secondary Minerals

During lateritic weathering the formation of new and secondary minerals constitutes an important phase. It is therefore of great importance to locate and identify the neo-mineralization. This helps in the study of chemistry of the weathering profile in terms of partitioning of elements and also in selecting the proper metallurgical procedures for extraction. With the devel-

opment of optical microscopy, electron microscopy, X-ray diffraction techniques, the cryptocrystalline characters of these secondary mineral phases have been studied in detail (e.g.: Kühnel et al., 1978; Chukrov, 1975; Esson and Carlos, 1978; Brindley, 1978). The surface area of such crystallites is extremely large and this determines the reaction rates during element concentration.

Brindley and Maksimovic (1974) and Brindley (1978) have systematically classified the hydrous nickel-containing silicates, ubiquitously present in the weathering profiles associated with nickeliferous laterites as follows:

1 : 1 layer type minerals	chrysotile-pecoraite lizardite-nopouite berthierine-brindleyite
2 : 1 layer type minerals	talc-willemsite kerolite-pinielite clinocllore-nimite sepiolite-falcondite

The term garnierite, following the recommendations of Pecora et al. (1949) and Faust (1966) is now accepted as a general term used widely when more descriptions cannot be given. Apart from this various other new mineral names such as nontronite, vermiculite and schuchardite are now in use. For detailed descriptions of the nomenclature of hydrous nickel silicates, the reader is referred to the work of Brindley and his co-workers (Brindley and Hang, 1973; Brindley and Maksimovic, 1974; Brindley and Wan, 1975; Brindley, 1978). The distribution of some of these secondary mineral phases in a weathering profile is illustrated in Figure 2.6.

Chemistry of Weathering of Ultra-basic Rocks

The change from a fresh ultrabasic rock to a fully formed laterite is a result of extensive geochemical remobilization and can be exemplified by the comparison of the chemical and mineralogical compositions of an average peridotite altered subsequently to a serpentinite and a laterite. The data in Table 2.4 obtained from the same bore-hole illustrate the degree to which chemical weathering alters a rock with the resulting remobilization and concentration of elements. Among the most striking features observed is the leaching out of magnesia and silica. It is of interest to note that these two oxides constitute nearly 80-90% of the original unweathered rock but in the end-product only about 1-2% remains - an indication of the extreme

leaching and accompanying remobilization. The descending meteoric waters contain carbonic and organic acids and these are responsible for the leaching out of some of the constituents of the original rock. The extreme leaching and concentration of the elements during the laterization of the ultrabasic rocks is illustrated in Figure 2.7. Alumina and also oxides of titanium are somewhat stable components of the parent rock and are generally used in the material balance composition.

Table 2.4. Chemical composition and mineralogical composition of average peridotite, serpentinite and laterite (after Kühnel et al., 1978; * from the same borehole; tr- traces)

Chemical Composition	Average Peridotite*	Serpentinite	Laterite
SiO ₂	43.9	43.2	1.84
TiO ₂	0.8	tr	0.14
Al ₂ O ₃	4.0	1.7	9.00
Fe ₂ O ₃	2.5	10.6	67.40
FeO	9.9		
NiO	0.2	2.8	1.50
MnO	0.1	0.2	0.80
MgO	34.3	32.4	0.80
CaO	3.5	tr	tr
Na ₂ O	0.6	tr	tr
K ₂ O	0.2	tr	tr
H ₂ O	-	13.9	14.22
Cr ₂ O ₃	0.3	0.2	3.77
S	tr	tr	tr
Cl	tr	tr	tr
Mineralogical Composition	Olivine Pyroxene Spinel Sulphide	Serpentine Spinel Hematite Goethite Magnesite Talc Clay mineral	Goethite Hematite Serpentine Spinel Clay Mineral Silica

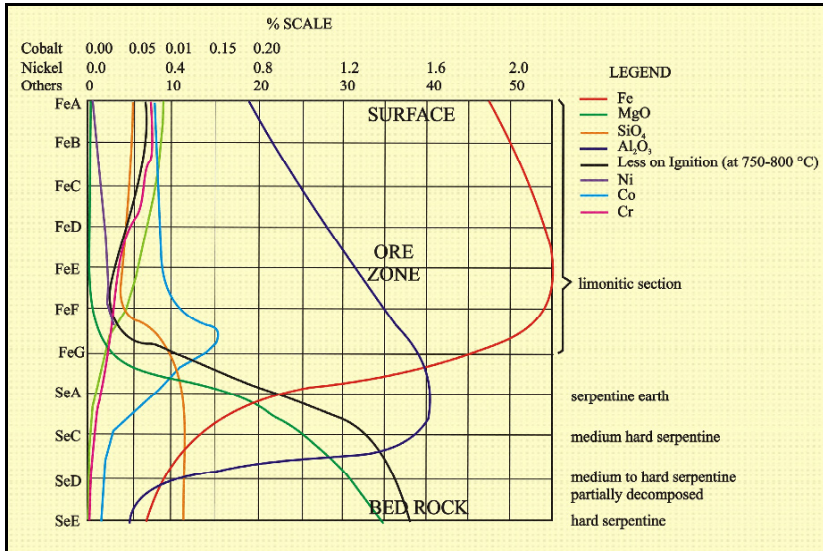


Fig. 2.7. Variation of elements with depth in a weathering profile over serpentinite (after de Vletter, 1978)

HYDROGEOCHEMISTRY OF THE TROPICAL ENVIRONMENT

The distribution of the different chemical species in the various components of the hydrological cycle has a marked influence on the medical geology of tropical lands, particularly in relation to groundwater related diseases.

Figure 2.8 illustrates the components of the shallow groundwater cycle that are sensitive to change. Several geochemical processes could take place in the groundwater cycle that could markedly alter the chemistry of the water. From among these the following processes are considered important:

- (a) evaporation and evapotranspiration,
- (b) selective uptake of ions by vegetation,
- (c) decay of organic matter,
- (d) weathering and dissolution of minerals,
- (e) precipitation of minerals,
- (f) mixing of different water qualities and
- (g) anthropogenic activities.

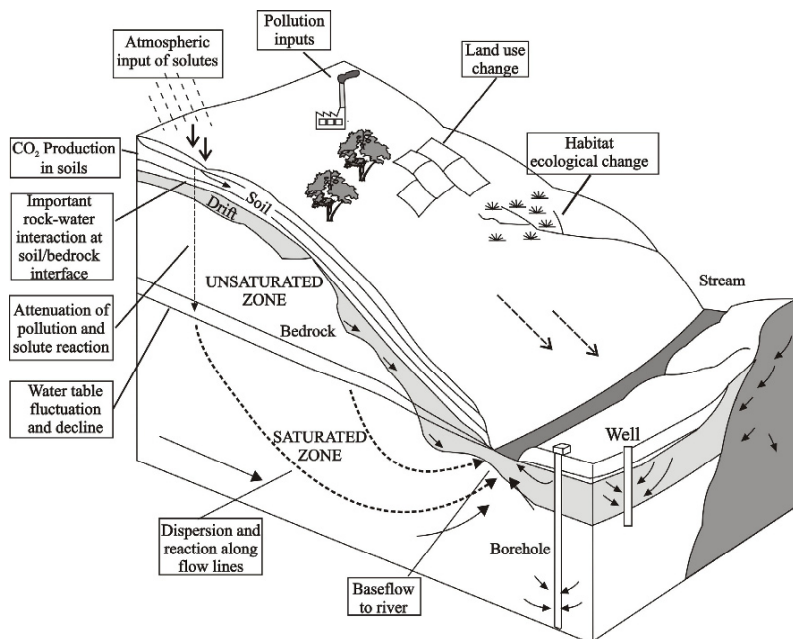


Fig. 2.8. Components of the shallow groundwater cycle showing elements that are sensitive to environmental change (Edmunds, 1996)

A schematic overview of the processes that affect water quality in the hydrological cycle is shown in Figure 2.9. Table 2.5 shows the processes which are important as sources of different ions and processes that may limit their concentration in fresh water. Trescases (1992) has shown that chemical elements are more likely to undergo pronounced fractionation in tropical environments than in temperate regions. The process of chemical separation, however, depends on their chemical mobility and the nature of the local environment. On account of this, tropical environments are far more likely to have areas with the potential for deficiency or toxicity conditions (Plant et al., 2000). The relative mobility of some essential and potentially toxic elements in different surface conditions is shown in Figure 2.10.

Table 2.5. Processes which are important as sources of different ions and processes that may limit their concentration ions in fresh water (after Appelo and Postma, 1994)

Elements	Process	Concentration Limits
Na ⁺	Dissolution, cation exchange in coastal aquifers	Kinetics of silicate weathering
K ⁺	Dissolution, adsorption, decomposition	Solubility of clay minerals, vegetation uptake
Mg ²⁺	Dissolution	Solubility of clay minerals
Ca ²⁺	Dissolution	Solubility of calcite
Cl ⁻	Evapotranspiration	None
HCO ₃ ⁻	Soil CO ₂ pressure, weathering	Organic matter decomposition
SO ₄ ²⁻	Dissolution, oxidation	Removal by reduction
NO ₃ ⁻	Oxidation	Uptake, removal by reduction
Si	Dissolution, adsorption	Chert, chalcedony solubility
Fe	Reduction	Redox-potential, Fe ³⁺ solubility, siderite, sulfide
PO ₄ ³⁻	Dissolution	Solubility of apatite, Fe, Al phosphates. Biological uptake

In an interesting study on the biogeohydrodynamics in a forested humid tropical environment in south Cameroon, Braun et al. (2002), perhaps for the first time world-wide, attempted to combine different approaches in hydrology, biogeochemistry, mineralogy, crystallography, microbiology, geophysics and pedology. One of the major results they obtained is the essential role played by the vegetation and soil organic matter in the fractionation, distribution or storage of the chemical elements in the humid tropical environment. They noted a strong geochemical contrast between the different groundwater zones-namely, flooded areas, hill slope lateritic profiles, weathering interface between the saprolite and the basement rocks and the swampy areas. Humic substances were particularly important in the weathering budget of elements usually considered as immobile in the surficial cycle, e.g.: Al, Th, Zr, and Fe.

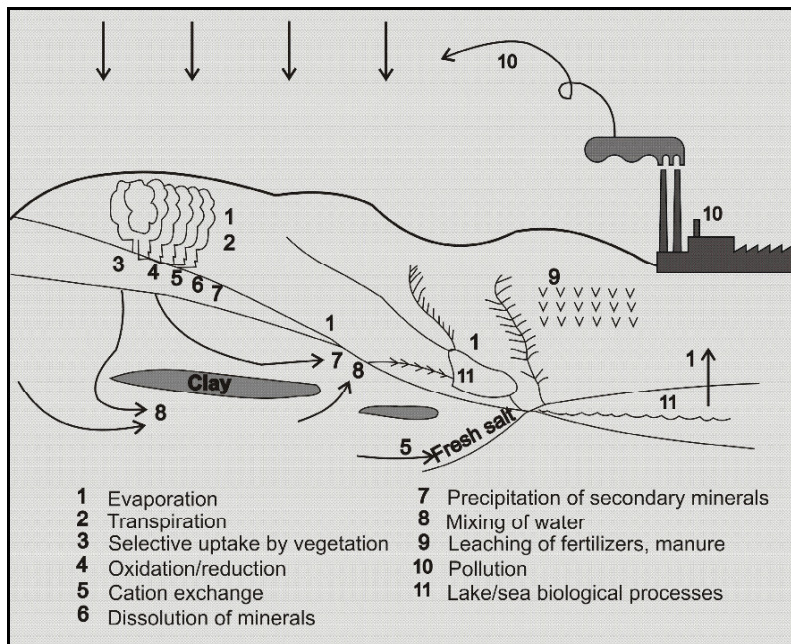


Fig. 2.9. A schematic overview of processes that affect the water quality in the hydrological cycle (Appelo and Postma, 1994)

The relatively high content of the oxygen containing functional groups such as CO_2H , phenolic and alcoholic OH , ketonic and quinonoid $\text{C}=\text{O}$ provide mechanisms for the easy interaction of organic soil and water constituents (Schnitzer, 1978). It is through the acid functional groups that these materials are thought to interact with metal ions to form metal-organic associations of widely differing chemical and biological characteristics.

Kerndorff and Schnitzer (1980) investigated the sorption of humic acid of metals from an aqueous solution containing Hg (II) , Fe (III) , Pb , Cu , Al , Ni , Cr (III) , Cd , Zn , Co and Mn with special emphasis on effects of pH, metal concentration and humic acid concentration. They observed that the sorption efficiency tended to increase with rise in pH, decrease in metal concentration and increase in humic acid contents of the equilibrating solution. The orders of sorption were as follows;

pH 2.4: $\text{Hg} > \text{Fe} > \text{Pb} > \text{Cu} = \text{Al} > \text{Ni} > \text{Cr} = \text{Zn} = \text{Cd} = \text{Co} = \text{Mn}$
 pH 3.7: $\text{Hg} = \text{Fe} > \text{Al} > \text{Pb} > \text{Cu} > \text{Cr} > \text{Cd} = \text{Zn} = \text{Ni} > \text{Mn}$
 pH 4.7: $\text{Hg} = \text{Fe} = \text{Pb} = \text{Cu} = \text{Al} = \text{Cr} > \text{Cd} > \text{Ni} = \text{Zn} > \text{Co} > \text{Mn}$
 pH 4.7: $\text{Hg} = \text{Fe} = \text{Pb} = \text{Al} = \text{Cr} = \text{Cu} > \text{Cd} > \text{Zn} > \text{Ni} > \text{Co} > \text{Mn}$

Relative Mobilities	Environmental Conditions		Environmental Conditions	
	Oxidising	Top Profile	Acid	Humid
Very High	I		↑	
High	Mo U Se F Ra Zn	Mo U Se F Ra Zn Cu Co Ni Hg		
Medium	Cu Co Ni Hg As Cd	As Cd		
Low	Pb Be Bi Sb Ti	Pb Be Bi Sb Ti Fe Mn		
Very Low	Fe Mn Al Cr	Al Cr		
Very Low	Al Cr Mo U Se Zn Co Cu Ni Hg	↓	Al Cr Zn Cu Co Ni Hg	Arid
Low	As Cd Pb Be Bi Sb Ti		Pb Be Bi Sb Ti Fe Mn	
Medium	Fe Mn		Ag Cd	
High	F Ra		F Ra	
Very High			Mo U Se	
Relative Mobilities	Reducing		Alkaline	

Fig. 2.10. The relative mobility of some essential and potentially toxic elements in different surface conditions (Plant et al., 2000)

The abundance and distribution of organic matter therefore plays a very significant role in a geochemical province where the element distribution shows a unique pattern. The water quality of groundwater in organic-rich soils will show special geochemical signatures as against groundwater in soil notably absent in organic matter.

In developing countries, many of which are in the equatorial humid tropical belt, the chemistry of the groundwater is of special importance in relation to medical geochemistry. The ground and surface water is often directly used as drinking water and the link between groundwater chemistry and health is obvious.

The groundwater derives its solutes from contact with various solids, liquids and gases as it finds its way from the recharge to the discharge area. The chemical composition of the rocks, mineral and soils through which the groundwater flows causes very large variations of the chemistry of the groundwater. In rural areas of the developing countries of the tropics,

particularly in areas where contamination due to industrial emission is minimal, the chemistry of the rocks, minerals and soils of a terrain is of paramount importance in the health of the indigenous people. Table 2.6 shows the concentration ranges of dissolved inorganic constituents in groundwater. These constituents are all ions except for aqueous silica. Minor and trace constituents of the water are far greater in number and anomalous situations occur when some of the trace elements shown in Table 2.6 reach very high concentrations and these would undoubtedly have an impact on the health of the people living in that area. Excess nitrates caused by heavy inputs of nitrogen-bearing fertilizers, heavy metals in acid soils around mineral deposits are examples. Iron is also known to show elevated concentrations around lakes, wet lands and in contaminant plumes (Kehew, 2001).

In the tropical environment, the water quality could be conveniently displayed in a piper diagram. It consists of two triangles one for cations and one for anions and a centrally located diamond-shaped figure. The concentrations of Ca, Mg and Na+K are on the three axes of the cation triangle. Similarly, Cl^- , SO_4^{2-} and $\text{CO}_2^- + \text{HCO}_3^-$ are plotted in the anion triangle. The water analysis depicted as a point in the two triangles is now projected onto the rectangle (Fig. 2.11).

The value of a piper diagram is further enhanced by its ability to classify the water types based on the water analyses plotted in the ion triangles. The water types also termed chemical facies, are illustrated in Figure 2.11. Medical geology has greatly benefited by the use of these Piper plots since geochemical provinces with their inherent water quality characteristics can be linked to problems of human and animal health. Such classifications of water types are particularly relevant to studies of the medical geology of cardiovascular diseases, where water hardness is a major factor.

In Bangladesh, a tropical humid country where leaching of soils is intense throughout the country, variability in climate causes variability in weathering rates. Islam et al. (2000) noted that spatial variability exists in the rate of mobilization/retention of both major and trace elements suggesting the importance of local controls. These authors noted that lakes and reservoirs are also generally enriched in all measured elements (Fig. 2.12), sometimes independently of the degree of depletion or enrichment of the soil profile. The study of Islam et al. (2000) in a tropical environment devastated by natural hazards, including adverse medical geochemistry (e.g. As, Al) is interesting from the point of view that it is not only the groundwater

that had received high inputs of major and trace elements, but surface water as well, compounding the drinking water problem of Bangladesh.

Table 2.6. Concentration ranges of dissolved inorganic constituents in groundwater (Freeze and Cherry, 1979; Davis and De Wiest, 1966)

Major constituents (greater than 5 mg/L)	
Bicarbonate	Silica
Calcium	Sodium
Chloride	Sulfate
Magnesium	
Minor constituents (0.01-10.0 mg/L)	
Boron	Nitrate
Carbonate	Potassium
Fluoride	Strontium
Iron	
Trace constituents (less than 0.1 mg/L)	
Aluminium	Molybdenum
Antimony	Nickel
Arsenic	Niobium
Barium	Phosphate
Beryllium	Platinum
Bismuth	Radium
Bromide	Rubidium
Cadmium	Ruthenium
Cerium	Scandium
Cesium	Selenium
Chromium	Silver
Cobalt	Thallium
Copper	Thorium
Gallium	Tin
Germanium	Titanium
Gold	Tungsten
Indium	Uranium
Iodide	Vanadium
Lanthanum	Ytterbium
Lead	Yttrium
Lithium	Zinc
Manganese	Zirconium

The chemical changes that occur in groundwater flow systems influence the hydrogeochemical anomalies that may be present locally and which may eventually have a bearing on the human and animal population. It has been observed (Chebotarev, 1955) that groundwater tends to evolve

chemically in long flow systems resulting in more concentrated solutions. As shown by Kehew (2000), this sequence is as follows:

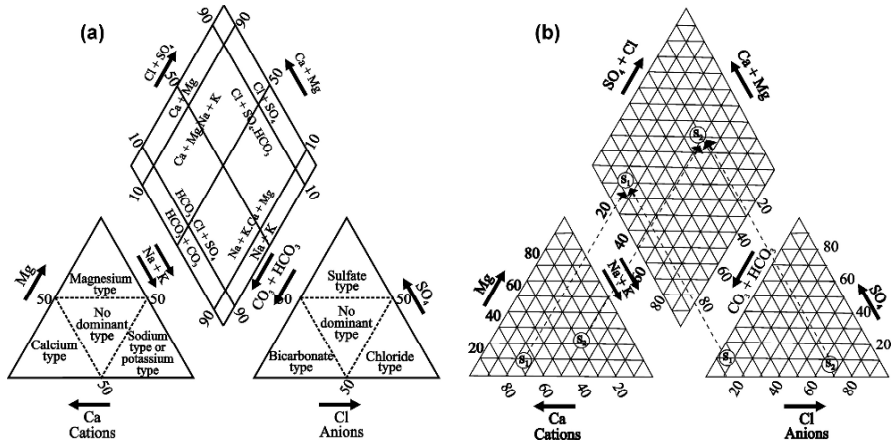


Fig. 2.11. (a) Classification of water types using the Piper trilinear diagram, (b) water analyses plotted on Piper trilinear diagram

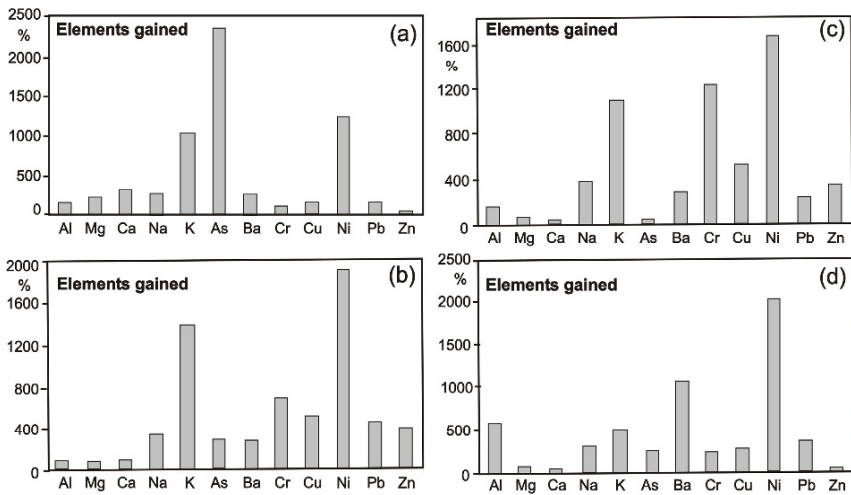


Fig. 2.12. Percent increase in dissolved elements in water of tropical environment in comparison to worldwide typical values: Rajarampur, b. Shamta, c. Mainamoti, d. Andulia (after Islam et al., 2000)

Tóth (1963) classified the groundwater flow systems as local, intermediate and regional flows systems, the size of each of them being governed by the topography in the drainage basin relative to the depth of the flow system. Figures 2.13 and 2.14 illustrate the distribution and hydrochemical facies of the different types of groundwater flow systems. From the point of view of medical geochemistry, the recharge and discharge areas are of significance in view of the hydrogeochemical anomalies that may be present at such localities, bearing in mind that the chemical composition of groundwater in flow paths that cross multiple rock types can be highly variable. Figure 2.15 shows such a scenario in a tropical environment in which the base rock mineralogy, soils, morphology and the ground water flow regime combine to form geochemical anomalies.

The presence of mineralization can also affect the groundwater quality of a terrain and this may have an impact on the health of the population living in such terrains. It is known that at depth, groundwater can transport ore and host elements both laterally and vertically. Exploration geochemists therefore use groundwater chemistry in regions where mineral deposits are deeply buried by a thick overburden as a tool in mineral exploration. The geochemical signatures from such buried mineralization are very often not amenable to most exploration techniques. The interaction of the groundwater within a body of mineralization brings about a change in the quality of groundwater chemistry. Groundwaters can therefore be used as pathfinders to concealed ore deposits. In an article published by the Australian Institute of Geoscientists (AIG, 2003), over 5500 groundwaters across mineral provinces of Australia have been sampled and the method applied.

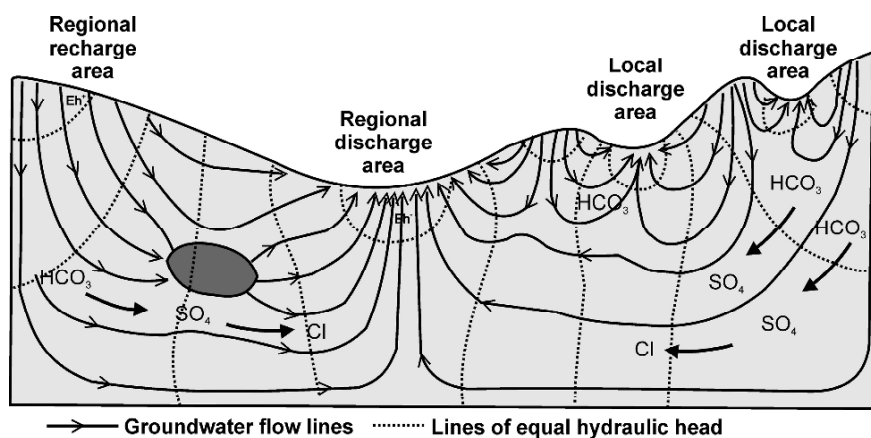


Fig. 2.13. Hydrochemical facies related to type of flow system in hypothetically regionally unconfined basin (Tóth, 1999)

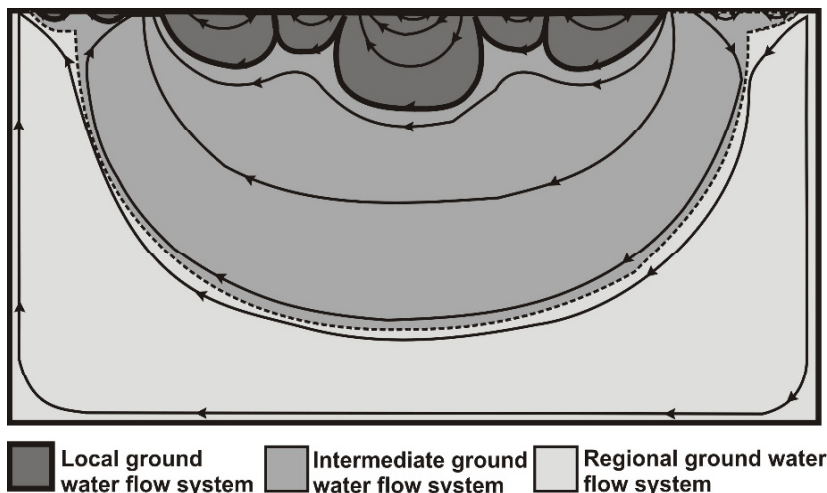


Fig. 2.14. Distribution of local, intermediate and regional groundwater flow systems in a drainage basin (Tóth, 1963, reproduced with kind permission from American Geophysical Union)

The field measurements include pH, Eh, salinity, temperature, reduced Fe, and trace elements. Geochemical anomalies observed from such geochemical exploration programmes for concealed mineralization can also be effectively used in projects aimed at delineating areas of anomalous trace element contents that could cause increased incidence of certain diseases. Areas underlain by granitic rock bodies may, for example, contain higher fluoride and rare-earth element concentrations and these may lead to diseases such as dental and skeletal fluorosis and endomyocardial fibrosis, among others. Further, the abundance of total dissolved solids (TDS), Ca and Mg carbonates, salinity etc in the water caused by the presence of rock types that enhance concentrations of such chemical components, may also have health implications.

A good understanding of the geology and the lithology of a terrain, its surface and groundwater chemistry, groundwater flow systems, their recharge and discharge areas and geomorphological aspects will be a useful prerequisite for any study concerning the epidemiology of an endemic disease such as those prevalent in tropical environments.

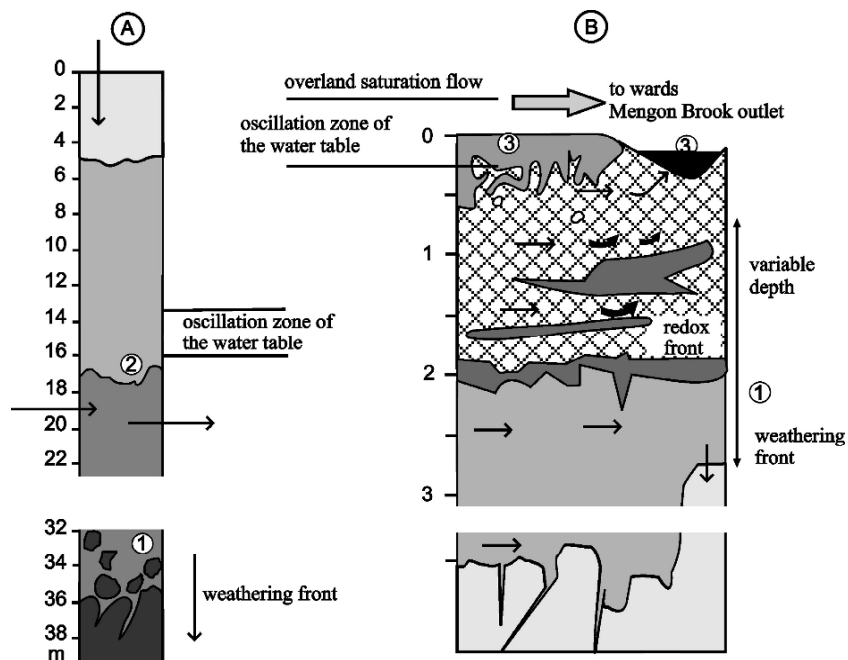


Fig. 2.15. Reference profile of a hill top (A) swamp (B) and location of the sampling waters. (1) Clear waters of the weathering front (2) clear water of the upper fringe of the hillside groundwater (3) coloured water of the surface groundwater and of the Mengong Brook (Braun et al., 2002)