Study Questions Exam 3

1. Name the four general types of soil colloids.

Layer aluminosilicates, amorphous aluminosilicates, AI and Fe oxides, and organic colloids (humus).

2. What are the three general types of layer silicate clay minerals?

Based on numbers of Si tetrahedral sheets and Al (or Mg) octahedral sheets, 1:1, 2:1 (2 Si tetrahedral sheets, 1 octahedral sheet in between) and 2:1:1 (same as 2:1 but with an additional, different type octahedral sheet).

3. What are the two basic building blocks (units of atoms in certain geometric configurations with respect to a central atom) of silicate clay minerals.

The Si tetrahedron and the AI (or Mg) octahedron.

4. How many silicon tetrahedral sheets and aluminum octahedral sheets are there in a 1:1 aluminosilicate clay? In a 2:1? In a 2:1:1?

See # 2 above.

5. Why don't 1:1 minerals expand when these are exposed to water?

The layer aluminisilicate minerals tend to occur stacked together. Consequently, the Si tetrahedral sheet of one crystal faces the octahedral sheet of its neighbor. In close proximity, therefore, are surface O atoms on the tetrahedral sheet and surface –OH groups of the octahedral sheet. The H of the –OH groups is H-bonded to the O, linking the neighboring crystals and preventing entry of water in the space (interlayer) in between neighboring crystals, hence, preventing expansion.

6. Of these general types of layer silicate minerals, only certain 2:1 minerals expand. Name the three general types of 2:1 minerals. Which is expanding? Which is limited-expanding? Which is non-expanding?

Smectite is expanding. Negative charge in the crystal lattice is mostly in the central octahedral sheet and while there is certainly attraction for interlayer cations by both of the neighboring crystals in the stacked configuration, the mutual attraction is not so strong as to prevent water from entering the interlayer region and expansion to occur.

In contrast, there is extensive negative charge (due to isomorphic substitution) in the tetrahedral sheets of illite and K balances this negative charge. The ionic radius of K is such that it can fit into partial voids in the surfaces of the tetrahedral sheets of adjacent illite crystals, bringing the – charges of adjacent crystals and + charges of K in close proximity, leading to strong mutual attraction and preventing expansion due to entry of water into interlayer spaces.

Vermiculite is intermediate in extent of isomorphic substitution and location of negative charge, leading to intermediate behavior. It is considered a limited-expanding mineral.

7. Explain why illite does not expand.

See # 6 above.

8. Are silicate clay minerals primary or secondary? Arrange 2:1 minerals, Al and Fe oxides and 1:1 minerals in their natural weathering sequence.

They are secondary, being chemically derived from primary minerals or formed from the dissolution products of primary minerals. As such, they are chemically more stable in the soil environment than primary minerals, however, there is a range of chemical stability among secondary minerals in the soil. The 2:1 minerals tend to form first from primary minerals and as these weather, 1:1 minerals form. The 1:1 minerals, however, are less stable than the AI and Fe oxides.

9. What kind of clay mineralogy might you expect in Honduras? In Ontario?

Assuming Honduras presents a harsh weathering environment and Ontario, a mild one --in Honduras, the end of this stability range, and in Ontario, the beginning.

10. What is isomorphic substitution? What charge occurs if Al³⁺ is substituted for Si⁴⁺? Does this occur in the octahedral sheet or tetrahedral sheet? What if Mg²⁺ substituted for Al³⁺? In which sheet does this substitution occur?

Isomorphic substitution is occurrence of a lower (or higher) valence cation than the cation that would occur in the idealized crystal lattice. This substitution happens during formation of the crystal lattice. For example, when AI^{3+} occurs where Si^{4+} would ideally occur in the tetrahedral sheet, there is a deficit of + charge (= excess of – charge). This substitution is possible because AI^{3+} has very nearly the same ionic radius as Si^{4+} (hence, "isomorphic"). Another common example is substitution of Mg2+ for Al3+ in the octahedral sheet, again leading to net – charge in the crystal lattice.

In minerals that have Mg (not AI) octahedral sheets, AI^{3+} may occur where Mg²⁺ would ideally occur. In contrast to the above, this is substitution of a higher valence cation for a lower valence cation, leading to net + charge in the crystal lattice (balanced by adsorption of – charge, anions, from solution). Minerals that have Mg octahedral sheets are called trioctahedral and have 3 Mg²⁺ atoms for every 2 Al³⁺ atoms that occur in minerals with AI octahedral sheets (called dioctahedral).

11. Is electrical charge due to isomorphic substitution permanent? What's the other type of charge on soil colloids called?

It obviously is since it is locked into the crystal lattice. pH-dependent, meaning that it varies with soil solution pH.

12. Explain how pH-dependent charge arises in mineral and organic colloids. What functional groups are involved?

Certain H-bearing functional groups will ionize a H (lose H^+ to solution), creating localized – sites, increasing the total – charge on the colloid. The tendency for this to occur increases with decreasing soil solution concentration of H^+ , i.e., with increasing pH (= -log[H⁺]). There are also functional groups that will bind H+ from solution, creating localized + sites. The tendency for this to occur increases with increasing soil solution concentration of H⁺, i.e., with decreasing pH. Both mineral and organic colloids exhibit pH-dependent charge. Some examples are:

$AI-OH = AI-O^{-} + H^{+}$	ionization of a mineral surface –OH group
$-COOH = -COO^{-} + H^{+}$	ionization of a carboxylic acid group in humus
$AI-OH + H^+ = AI-OH_2^+$	protonation of a mineral surface –OH group
$-NH_2 + H^+ = -NH_3^+$	protonation of an amino group in humus

where the = is supposed to mean equilibrium reaction

13. Define cation exchange capacity (CEC). Define AEC.

CEC is the sum of extractable cations (acidic and basic) per unit mass of soil. It is equal to the – charge on soil colloids. AEC is the sum of extractable anions and is equal to the + charge. Both are methodologically defined.

Depending on how one goes about extracting cations, different values for the CEC are determined. One can, for example, extract base cations like in lab using ammonium acetate (NH₄OAc), and use a separate method to extract and quantify acid cations (as described in the lab manual). This approach leads to the highest value for CEC. Alternatively, one can just use NH₄OAc, then follow this with an extraction of NH₄⁺ and determine the quantity of NH₄⁺ that was adsorbed in the original extraction procedure.

Since NH_4^+ is not a highly effective extractant for AI^{3+} and H^+ , this procedure leads to a lower estimate of CEC. There is also another approach that is supposed to give what is called the "effective CEC", but it is even lower.

14. What happens to CEC as pH increases? What happens to AEC as pH decreases?

See # 12. CEC increases as pH increases since the amount of pH-dependent – charge increases. The opposite is true for AEC, the amount of pH-dependent + charge increases as pH decreases.

15. Given data (millimol (+) / 100 g_{soil} or cmol (+) / kg_{soil}) for basic cations and acidic cations in a soil, be able to calculate the CEC. Also, be able to calculate the percentage base saturation (% BS).

You can do this. No problem.

16. What is the general relationship between pH and % BS?

Crudely, as the % BS (% of CEC composed of base cations) increases, the % of the CEC due to acid cations decreases. With fewer acid cations, the overall system is less acid, there is a lower concentration of acid cations in the surrounding soil solution and it has a higher pH. Thus, pH is positively correlated with % BS. The actual functional relationship, pH = f (%BS), is generally sigmoidal in shape. See examples.

17. Rank kaolinite (a 1:1 mineral), illite, smectite and vermiculite in order of decreasing CEC. Assuming neutral soil pH, how does the CEC of humus compare to the highest CEC mineral colloid?

See table from text or elsewhere. CEC of humus (~ 200 cmole+ / kg) > vermiculite (~ 150) > smectite (~ 100) > illite (~ 20) > kaolinite (~ 5). Note that although illite has a lot of isomorphic substitution, the greater majority of this – charge is balance by interlayer K+, which is not extractable and, therefore, does not measurable as CEC.

18. Knowing what you do about the CECs of different colloids and that there is such a thing as pH-dependent charge, what are three factors that determine the CEC of a soil?

Types of colloids, quantity of these and solution pH.

19. Write a balanced equation that represents the cation exchange of solution phase K^+ for adsorbed Ca²⁺.

There are lots of different ways to represent this. One way is,

 $Ca^{2+}_{ads} + 2K^{+} = 2K^{+}_{ads} + Ca^{2+}$

where the subscript ads is to read adsorbed onto colloid surface and absence of subscript means in solution. Regardless of how you do it, the reaction must be balanced in mass and charge.

- 20. Cation exchange in soils is (slow / rapid) and (reversible / irreversible).
- 21. Explain why 1 N NH₄OAc (ammonium acetate) is used to displaced adsorbed basic cations in measurements of CEC. Would 0.01 N NH₄OAc be equally effective?

Look at # 19. It is an equilibrium reaction, meaning that it does not go to completion. Regardless of how concentrated is K^+ in solution (left hand side, LHS), there will always remain some adsorbed Ca²⁺, however, with increasing concentration of K^+ , there will be less and less remaining adsorbed Ca²⁺. The same idea holds here –a 1N (= 1M) solution of NH₄⁺ is much more effective in displacing adsorbed cations than a 0.01 N one, and, in fact, leads to almost complete extraction of initially adsorbed base cations (though not that effective for the acid ones).

Why isn't 1 N NH₄OAc used in an extraction procedure to measure acidic cations?

Besides the greater strength of adsorption of the acid cations (see # 22), the H⁺ and Al³⁺ that is desorbed (displaced) by NH_4^+ cannot be measured. The NH_4OAc is a buffered solution (typically pH = 7), so desorbed H⁺ cannot be directly measured and desorbed Al³⁺ tends to be precipitated from solution

22. Arrange Na⁺, K⁺, Al³⁺, Mg²⁺, Ca²⁺ and H⁺ in order of decreasing affinity (strength) of adsorption onto soil colloids.

Approximately, AI^{3+} and $H^+ > Ca^{2+}$ and $Mg^{2+} > K^+$ and Na^+ . See a pattern except for the highly reactive, oddball H^+ ?

23. Why is Al³⁺ considered an acidic cation?

It hydrolyzes in solution to generate H^+ , e.g., $AI^{3+} + H_2O = AIOH^{2+} + H^+$.

24. Why do humid region soils tend to become acidic?

The soil is alive with organisms that give off CO_2 and consume organic matter. The CO_2 forms H_2CO_3 which ionizes to give H⁺. Decomposition of organic matter releases organic acids and the oxidation of S and N released from organic matter during decomposition gives H_2SO_4 and HNO_3 . Thus, there is H⁺ produced in the soil and it is an exchangeable cation that tends to displace base cations that are adsorbed on soil colloids. Once these base cations are in solution, they are subject to leaching (the premise is that it is a humid region with water percolation). This, clearly, leads to reduced % BS and reduced pH of the system.

This natural acidification process is slowed by plant uptake of base cations and their return to the soil surface with plant residue and leaching of plant foliage. To some extent, there is also some atmospheric deposition of base cations. However, neither rate of nutrient cycling nor atmospheric deposition keeps up with leaching rate and soils tend to acidify with time.

25. The concentration of H⁺ in the soil solution is 0.00001 M. What is the pH? Is this soil acid, neutral or basic? What is the concentration of OH⁻?

See # 12 for pH definition. pH = 5. Acid. $[H^+][OH^-] = 10^{-14}$. Therefore, $[OH^-] = 10^{-9}$.

26. What is the source of acidity in distinctly acid soils, say pH < 5? What about in more mildly acid soils, say pH 5 to 6.5?

Exchangeable H^+ and AI^{3+} in very acid soils. In less acid soils, some exchangeable H^+ remains but the remaining exchangeable AI exists in some hydrolyzed form, like AIOH²⁺.

27. What is the source of OH⁻ in alkaline soils.

These soils have carbonate, $CO_3^{2^-}$, and bicarbonate, HCO_3^- . Both hydrolyze to generate OH⁻, e.g., $CO_3^{2^-} + H2O = H_2CO_3 + 2OH^-$.

28. From the standpoint of plant growth, what is the usual optimum range in soil pH?

5.5 or 6.0 to 7.0. But some plants do better under more acid or basic conditions.

29. What is active acidity? Exchangeable? Residual?

Active = solution H^+ , exchangeable = adsorbed, exchangeable H^+ and AI^{3+} (and other forms), and residual = strongly adsorbed, bound H^+ and AI^{3+} (and other forms). These pools together are total acidity. Active acidity contributes little to total acidity.

30. List several ways by which soil pH is altered.

Soils naturally acidify (see # 24). If one adds an NH_4^+ -containing fertilizer, e.g., $NH_4(SO4)_2$, the NH_4^+ is largely oxidized by certain bacteria in the soil to form HNO_3 (nitric acid). Aeration of a soil that contains chemically reduced S (like a wetland, anaerobic soil where $SO_4^{2^-}$ [sulfate] has previously been used by certain anaerobic microbes as a terminal electron acceptor in their respiration and H_2S has been produced), will result in its oxidation to H_2SO_4 , sulfuric acid. Addition of organic matter is an extra source of H_2CO_3 (carbonic acid), various organic acids, HNO_3 and H_2SO_4 as the organic matter is decomposed.

Of course one may lime a soil to increase pH. One may also, unintentionally, add sufficient Na, without Ca, to increase the % BS and pH. In the absence of Ca (or with very little Ca present in the soil), Ca does not precipitate with $CO_3^{2^-}$ and the pH of the soil solution is not controlled by CaCO3 equilibrium (setting the pH ~ 8.5). Rather, the pH continues to climb with increasing % BS and very plant-unhealthy pHs arise.

31. What is pH buffering? What reactions buffer soil pH when base is added to an acid soil? When acid is added to an alkaline soil?

pH buffering refers to the tendency of a system to resist a change in pH upon introduction of acid or base. For example, when base is added to an acid soil, OH- + H+ = H20 or 3OH- + Al3+ = Al(OH)3, a precipitated mineral. Thus, some or all of the added base is consumed. However, even if all the base were consumed, the reduction in the content of H+ and Al3+ would lower the total quantity of acid present and the pH would rise to some extent.

When acid is added to an alkaline soil, $2H^+ + CO_3^{2-} = CO_2 + H_2O$. Depending on whether sufficient H^+ is added to consume all carbonate and whether the system is buffered by the presence of CaCO₃, the pH may or may not change.

32. What is shown by a soil buffer curve?

pH as a function of % BS. It increases as % BS increases.

33. Name three types of lime materials.

Carbonates (e.g., $CaCO_3$), hydroxides (e.g., $Ca(OH)_2$) and oxides (CaO). Mg as well as Ca forms.

Gypsum, CaSO₄ (actually the dehydrate form) is not considered a lime material. However, it has been used to decrease subsoil acidity because it is much more mobile in the soil than lime materials. Thus, it can leach into the subsoil where the Ca exchanges with adsorbed acid cations, subjecting them to leaching, and increasing the % BS. The sulfate component also has a minor effect on increasing soil pH. 34. What material is commonly used to lower soil pH?

Sulfur, $S + 1.5O_2 + H_2O = H_2SO_4$. This occurs slowly abiotically (chemically) but quickly through the action of certain bacteria that obtain energy in this way.

35. Let's say you have found that it takes 1.0 meq of OH^{-} per 10 g of soil to raise the pH from 5.0 to 6.6, how many Mg of $CaCO_3$ do you need to add to the HFS. The milliequivalent weight of $CaCO_3$ is 50 mg. Assume a HFS has a mass of 2000 Mg. How many tons of $CaCO_3$ per AFS (1000 tons per AFS)?

(1.0 mmole_{OH-} / 10 g_{soil}) x (50 mg_{CaCO3} / 1 mmole_{OH-}) x (0.001 g / 1 mg) x

 $(2000 \text{ Mg} / \text{HFS}) = 10 \text{ Mg}_{CaCO3} / \text{HFS}$

Solve this type problem by knowing the mass of lime material that is chemically equivalent to 1 mmole_{OH-} in its capacity to neutralize H^+ . The product of the first 3 terms in the above expression give the ratio of mass of lime material to mass of soil needed to effect the pH increase. The 4th term is the mass of soil, which when multiplied by the first 3, gives the total mass of lime material needed.

36. Question 35 refers to soil A. Soil B has exactly the same shape buffer curve as soil A. It, too, is initially at pH 5.0 and you want to raise the pH to 6.6. However, the CEC of soil B is twice the CEC of soil A. Would you need to add more or less lime to soil B than to soil A? About how much lime would be needed for soil B?

The same increase in % BS is needed for both soils. Since the CEC of $B = 2 \times CEC$ of A, twice as much lime is needed for B as A

37. Soil tests show that you need to add 1 ton of finely ground limestone per acre to adjust the soil pH of 10 acre contaminated site for optimal microbial degradation activity. Having a cushy budget and knowing that CaO is faster reacting, you opt for it instead of the limestone. How much do you apply?

You can write neutralization reactions like,

 $CaCO_3 + 2H^+ = Ca^{2+} + CO_2 + H_2O$

 $CaO + 2H^+ = Ca^{2+} + H_2O$

showing that one mole of $CaCO_3$ and one mole of CaO consume the same amount of H⁺, 2 moles. A mole of CaO weighs a fraction of a mole of CaCO3. In fact, it weights

 $MW_{CaO} / MW_{CaCO3} = 56 / 100 = 0.56$ of a mole of CaCO₃. Consequently, 0.56 tons CaO would be required if 1 ton of CaCO₃ was required.

- 38. Liming is a once in a life-time, permanent correction of soil acidity (True / False).
- 39. What effect does soil salinity have on plant uptake of water?

With respect to plant uptake of water, the total potential = matric + osmotic potentials in an unsaturated soil (gravitational potential is irrelevant to the matter, yes?). As a soil dries, its matric potential becomes increasingly negative. The higher the concentration of salts in the soil solution, the more negative is the osmotic potential. Plant uptake of water requires that the water potential in the root be less than the water potential in the surrounding soil. Thus, the presence of salts, making the water potential of the soil solution more negative than it would be in their absence, means that the plant stops uptaking water at a higher (less negative) matric potential, i.e., when the soil is wetter.

40. Tendency for soil salinization is greatest under which set of conditions

Factor	A	В	С	D
Irrigation water	Saline	Non-saline	Saline	Non-saline
Soil drainage	Good	Good	Poor	Poor

41. What is used as a measure of soil salinity? What are two measures sodicity (Na content)?

Electrical conductivity, EC (dS / m). ESP (exchangeable Na % = % fraction of the CEC composed of Na) and SAR (Na adsorption ratio, the ratio of Na in solution to the square root of the average of Ca and Mg in solution). The latter is empirically and directly related to ESP and much easier to measure on a routine basis (soil testing lab). Consequently, it has supplanted ESP as a measure of sodicity.

42. Soils A and B are both alkaline. There is a whopping lot of Ca in soil A but not much Na. The composition of soil B is just the opposite, a lot of Na, not much Ca. Which likely has the higher pH?

Soil B. Both have high % BS but there is likely insufficient Ca in it that $CaCO_3$ buffers the pH at ~ 8.5. It's pH may be much higher than this.

43. Define saline, sodic and saline-sodic soils based on EC and SAR.

Saline, EC > / = 4 dS / m but SAR < 13 (or ESP < 15 %)

Sodic, EC < 4 but SAR > / = 13 (or ESP > / = 15 %)

Saline-sodic, EC > / = 4 and SAR > / = 13 (or ESP > / = 15 %)

44. How does the salt in white alkali soils get to the surface?

It is deposited there when water that has moved to the surface evaporates.

45. What causes the black in black alkali soils?

This is a sodic soil with dispersed soil colloids, including organic colloids (humus). The dispersed humus is suspended or dissolved in the soil solution. Like with salts in # 44, it is carried to the soil surface with the evaporation stream and is deposited there.

46. Why is the hydraulic conductivity of sodic soils lousy?

Colloids, including mineral, are dispersed, resulting in much smaller soil pores and much smaller hydraulic conductivity.

47. What happens if you try to flush excess salts from a saline-sodic soil using water of low salt concentration? So in which case (saline, sodic or saline-sodic) is this the proper reclamation strategy?

It is an interesting phenomenon that a soil loaded with Na can yet have normal hydraulic conductivity if the concentration of salts in the soil solution is high (saline-sodic soil). Let's see if I can explain.

Ca (dropping scripts for ease) is more strongly adsorbed than Na (see # 22) and more closely adsorbed to surfaces of colloidal particles. In the absence of any adsorbed cations (an impossible situation but one which we can imagine), the negatively charged colloidal particles would all mutually repel and be perfectly dispersed. The presence of surface adsorbed cations prevents this, however, some cations are more effective (e.g., Ca) in shielding or blocking effects of the mutually repulsive negative colloidal charges than others (e.g., Na) due to charge per cation and proximity to colloidal surface. If we compare the repulsive effect in a Ca-saturated system (only Ca adsorbed and in solution) and in a Na-saturated system, it is less in the Ca system and the colloidal particles can more closely approach one another.

Total concentration of cations in solution is also a factor in this. The higher the concentration of cations in solution (hence, concentration of shielding positive charge), the further minimized is repulsion among negatively charged colloidal particles. It is possible, therefore, for a system with a high concentration of Na relative to Ca to exhibit negligible repulsion among colloidal particles if the concentration of cations is sufficiently high (high salt concentration). Even though Na is considered a dispersing cation, if its solution concentration is high, it can flocculate colloidal particles. On the other hand, even though Ca is considered a flocculating cation, if its solution concentration the Ca system will tend to be flocculated but a Na system will tend to be dispersed.

So, a saline-sodic soil has sufficiently high salt concentration that colloidal particles are not dispersed despite high Na content. But reduce the concentration of salts in solution by flushing with low-salt water and you induce dispersion. You obviously can't improve a sodic soil by flushing with low-salt water because you do nothing to reduce the level of adsorbed Na and, furthermore, you can't get water to flow through it due to its poor conductivity. This is a long explanation to the answer –a saline soil.

48. How do you reclaim a sodic or saline-sodic soil?

You add a flocculating cation or flocculating cation, then flush. Typically, Ca is added as gypsum. The Ca, being preferentially adsorbed to Na, will flocculate colloidal particles in a sodic soil or ensure that colloidal particles do not disperse when a saline-sodic soil is subsequently flushed. Some of the added Ca will also precipitate carbonate and the pH will adjust downward to ~ 8.5, improving the chemical fertility.

49. List three benefits of earthworms.

Aid decomposition of organic matter (render it more labile to microbial decomposition), improve water infiltration (burrows open to the surface = open macropores), improve internal drainage (burrow macropores), and aeration (burrow macropores).

50. In what way do certain nematodes adversely affect plants?

Create wounds in roots through which pathogens gain access. Roots stunted and overall growth and productivity hurt.

51. Explain why the rhizosphere is biologically and chemically different from the bulk soil.

The rhizosphere is that part of the soil immediate to the root. It is enriched with root exudates (various organics) and cells lost from the root. Consequently, the rhizosphere is enriched with substrates microorganisms can readily use, so it exhibits a larger, more active population of microorganisms.

52. What group of soil microflora is typically the most numerous? Which often has the greatest biomass?

Bacteria. Fungi.

53. Which three groups of soil microflora are principally responsible for organic matter decomposition?

Bacteria, actinomycetes and fungi.

54. What are three types of fungi?

Molds, mushrooms and yeasts.

55. What are the mutual benefits derived by plants and fungi in mycorrhizal associations? What are the two most general types of mycorrhizae?

The fungi get access to photosynthetic products of the plant. The plant has access to nutrients uptaken by the fungal hyphae. The latter is especially a benefit with respect to nutrients are immobile in the soil and in a soil that is infertile.

- 56. Ectomycorrhizal hyphae invade root cells (True / False).
- 57. What are three general groups (based on morphology) of bacteria?

Cocci (spherical), bacilli (rod) and spirilla (spiral).

58. List several important reactions carried out by certain soil bacteria.

We'll deal with this in more detail shortly. As for now, biological N-fixation (atmospheric N₂ reduced to ammonia and bound into organics), nitrification (oxidation of NH_4^+ to NO_3^- with release of H^+), denitrification (use of NO_3^- as a terminal electron acceptor by certain anaerobic microbes with its conversion to various gaseous forms of N, ultimately N₂), and S oxidation to H_2SO_4 .

59. In regard to soil microbial activity, what do the terms mineralization and immobilization mean? Which is good for plant nutrition, net mineralization or net immobilization?

Mineralization means release of organically-bound N, P and S in simple, plant-available inorganic forms such as NH_4^+ . Immobilization is the uptake of such simple inorganic forms and their incorporation into organic molecules, i.e., the opposite. Net mineralization.