Rainwater pH

a) $pCO_2 = 1.6*10^{-4} atm = 10^{-3.7959} atm$
25ºC

$$k_H = 3.39*10^{-2} \frac{mol}{barL} * \frac{bar}{0.9869atm}$$

$$= 0.0335 \frac{mol}{atmL}$$

$$= 10^{-1.4755} \frac{mol}{atmL}$$

$$[CO_{2(aq)}] = 10^{-1.4755-3.7959}$$

$$= 10^{-5.2714} M$$

15ºC

$$k_H = 4.55*10^{-2} \frac{mol}{barL} * \frac{bar}{0.9869atm}$$

$$= 4.449*10^{-2} \frac{mol}{atmL}$$

$$= 10^{-1.3477} \frac{mol}{atmL}$$

$$[CO_{2(aq)}] = 10^{-1.3477-3.7959}$$

$$= 10^{-5.1436} M$$

b)

$$\log_{10} k = \frac{-\Delta_r G^{\underline{o}}}{2.303RT}$$

$$-\Delta_r G^{\underline{o}} = -(-586.8kJ/mol - (-623.2kJ/mol))$$

$$= 36.4kJ/mol$$

$$\log_{10} k = -\frac{36.4}{5.708}$$

$$= -6.3770$$

$$k = 10^{-6.3770}$$

c)

$$\log_{10} k_{15ºC} = \log_{10} k_{25ºC} + \frac{-\Delta H^{\underline{o}}}{2.303RT}(\frac{1}{T_{25ºC}} - \frac{1}{T_{15ºC}})$$

$$= -6.3770 + \frac{-689.93kJ/mol + 699.09kJ/mol}{2.303(8.314J/(molK))}(\frac{1}{298.15K} - \frac{1}{288.15K})$$

$$= -6.3770 + \frac{9160J/mol}{19.1471J/(molK)}(-0.000116398K)$$

$$= -6.4327$$

d)
25ºC

$$[H^+]^2 = 10^{-6.3770-5.2714}$$

$$= 10^{-11.6484}$$

$$[H^+] = 10^{-5.8242}$$

$$pH = 5.82$$

15°C

$$[H^+]^2 = 10^{-6.4327-5.1436}$$
$$= 10^{-11.5763}$$
$$[H^+] = 10^{-5.7881}$$
$$pH = 5.79$$

Groundwater

a) Rocks and minerals are dissolved by groundwater as it seeps through the ground and percolates through. Groundwaters have been in contact with greater amounts of rocks and minerals than surface water, allowing for great solvation. Groundwater at greater depths have been in contact with a greater amount of rocks and minerals.

b)

$$SI = \log_{10} \frac{IAP}{k_{sp(calcite)}}$$
$$= \log_{10} \frac{1.6 * 10^{-3} mol L^{-1} * 4 * 10^{-6} mol L^{-1}}{3.36 * 10^{-9} mol^2 L^{-2}}$$
$$= \log_{10} 1.9048$$
$$= 0.2798 \,|\, 0.18$$
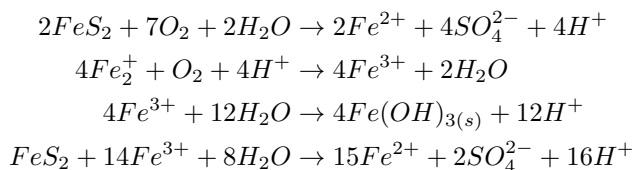
The groundwater is supersaturated with respect to calcite, so additional calcite is not dissolving.

c)

$$SI = \log_{10} \frac{IAP}{k_{sp(calcite)}}$$
$$= \log_{10} \frac{1.6 * 10^{-4} mol L^{-1} * 1.1 * 10^{-6} mol L^{-1}}{3.36 * 10^{-9} mol^2 L^{-2}}$$
$$= \log_{10} 0.0524$$
$$= -1.2807 \,|\, -1.38$$

After the increase in human activity, the water has become undersaturated with respect to calcite. This is because the groundwater which was supersaturated in calcite was removed, and fresher surface water percolated down. This new water is not saturated, so it will dissolved calcite. If this removal cycle continues, calcite will be removed. Once a small defect forms, more water can flush through the region, forming sinkholes in regions with extensive carbonate bedrocks.

d) Pyrite dissolution is environmentally hazardous because the oxidation of pyrite produces a large amount of sulfuric acid, acidifying water. This is a major concern in areas with abandoned coal mines because pyrite is commonly associated with coal deposits. The elevated acidity can also cause the dissolution of other metals into the water. The very acidic water is usually devoid of aquatic life, and the acidity may even kill nearby trees. There have been many attempts to counteract this problem. Aerobic and anaerobic wetlands have been constructed in hopes that bacteria and other organisms will be able to help neutralize the acidity. Other engineering projects have focused on a more active resolution through the use of limestone to neutralize the acid. Open limestone channels neutralize water flowing through, while diversion wells actively mix acidic water with crushed limestone. Unfortunately, metals such as iron quickly come out of the water and coat the limestone. An anoxic limestone drain attempts to keep oxygen out and prevent this oxidative armouring of limestone by metals.

$$2FeS_2 + 7O_2 + 2H_2O \rightarrow 2Fe^{2+} + 4SO_4^{2-} + 4H^+$$
$$4Fe_2^+ + O_2 + 4H^+ \rightarrow 4Fe^{3+} + 2H_2O$$
$$4Fe^{3+} + 12H_2O \rightarrow 4Fe(OH)_{3(s)} + 12H^+$$
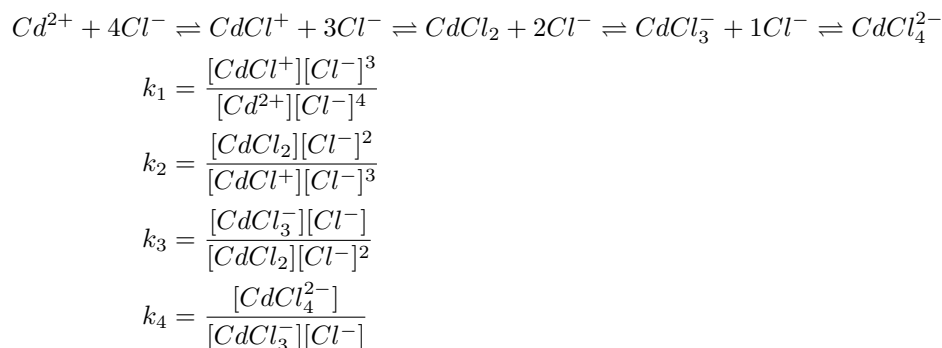$$FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+$$

The second step involving direction oxidation by dioxygen is the rate determining step. This is especially problematic because industrial processes turn pyrite into fine crystals and dust, increasing the surface area and adsorption of dioxygen onto pyrite.

Cadmium discharge

a) As the cadmium moves from the river into an estuary and finally is dischaged to sea, it will encounter increasing amounts of chloride anion. As the concentration of chloride increasing, cadmium will become increasingly complexed with chloride, complexing with up to four chlorides and turning from a cadmium metal cation to a complexed anion.
b) After measuring the total amount of cadmium, the cadmium speciation would have to be taken into account. This could be done by measuring the chloride concentration of the water sample as well, and then referencing the species distribution. Because increasing complexation with chloride decreases toxicity, two water samples which may have the same cadmium concentration may have different toxicities; the sample with higher chloride concentration may have lower cadmium toxicity.
c)

$$Cd^{2+} + 4Cl^- \rightleftharpoons CdCl^+ + 3Cl^- \rightleftharpoons CdCl_2 + 2Cl^- \rightleftharpoons CdCl_3^- + 1Cl^- \rightleftharpoons CdCl_4^{2-}$$

$$k_1 = \frac{[CdCl^+][Cl^-]^3}{[Cd^{2+}][Cl^-]^4}$$

$$k_2 = \frac{[CdCl_2][Cl^-]^2}{[CdCl^+][Cl^-]^3}$$

$$k_3 = \frac{[CdCl_3^-][Cl^-]}{[CdCl_2][Cl^-]^2}$$

$$k_4 = \frac{[CdCl_4^{2-}]}{[CdCl_3^-][Cl^-]}$$

Anhydrite dissolution

a)

$$\log_{10} k_{sp(anhydrite)} = \frac{-(-553.6kJ/mol + -744.0kJ/mol - -1321.8kJ/mol}{5.708kJ/mol}$$

$$= \frac{24.2}{5.708}$$

$$= -4.23966$$

$$k_{sp(anhydrite)} = 10^{-4.23966}$$

b)

$$k_{sp} = 10^{-4.23966}$$

$$= [Ca^{2+}][SO_4^{2-}]$$

$$[Ca^{2+}] = 10^{-2.12}M$$

c)

$$\alpha_i = \gamma_i M_i$$

$$k_{sp} = \gamma_{Ca}[Ca^{2+}]\gamma_{SO_4^{2-}}[SO_4^{2-}]$$

$$[Ca^{2+}][SO_4^{2-}] = \frac{k_{sp}}{\gamma_{Ca}\gamma_{SO_4^{2-}}}$$

If the activity, apparent concentration, is assumed to be equal to the actual concentration, then γ_{Ca} and $\gamma_{SO_4^{2-}}$ are equal to unity. However, if the apparent concentration of each ion is lower than the actual concentration, then $\gamma_{Ca}\gamma_{SO_4^{2-}} < 1$, and dividing a value by a number $(0, 1)$ will increase the value.