Abstract

In this chapter we concentrate on the chemical and biogeochemical processes involved in the anthropogenic generation of acidity and its transfer through the atmosphere to the terrestrial and aquatic environment. Unifying definitions of acid- and base-neutralizing capacity (alkalinity and acidity) are helpful in appreciating the major \( H^+ \) yielding and \( H^+ \) consuming processes occurring in the atmosphere, in the watersheds, and in the lake. Because the transfer of electrons is coupled with the transfer of protons, oxidation and reduction are accompanied by proton release and proton consumption. Among the redox processes that have a major impact on \( H^+ \) balance are the synthesis and mineralization of biomass. Any uncoupling between photosynthesis and respiration affects acidity and alkalinity in terrestrial and aquatic ecosystems. In the watershed, aggrading vegetation (forests and intensive crop production) produces acidity; chemical weathering, on the other hand, neutralizes inputs of acids by atmospheric deposition and internal acidity production. Models to estimate the critical load of acid deposition that can be neutralized by the ecosystem without causing deleterious biological effects are currently under development. Two case studies are reviewed briefly: (1) acid alpine lakes, where acid deposition is neutralized partially by chemical weathering of crystalline rocks, and (2) a large-scale watershed manipulation in which the stream has been acidified by the addition of \( (NH_4)_2SO_4 \) via uptake of ammonium by vegetation and nitrification with the export of nitrate and sulfate evident in the streamwater.

The latter case is an example of a forested catchment exhibiting nitrogen saturation.

1 Introduction: Anthropogenic Generation of Acidity

Acid atmospheric deposition results from the disturbance of cycles that couple atmosphere, land, and water. The surface of our environment is in a global sense on the average with regard to a proton and electron balance in a stationary state. Considering the Goldschmidt reaction in its most simple scheme

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\text{igneous rock} + \text{volatile substances} \rightleftharpoons \text{air} + \text{seawater} + \text{sediments. (1)}
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Sillén (1961) gave the picture that volatiles (\( H_2O, CO_2, HCl, \) and \( SO_2 \)), the acids of volcanoes (i.e., the acids that have leaked from the interior of the earth) have reacted in a gigatic acid base reaction with the bases of rocks (silicates, oxides, and carbonates). Similarly, he calculated from a model system the quantities of redox components that have participated in a redox titration. The present day stationary state with regard to \( H^+ \) and \( e^- \) balance is reflected in an atmosphere with 20.9% \( O_2 \), 0.03% \( CO_2 \), and 79.1% \( N_2 \), as well as a world ocean with pH \( \approx 8 \) and \( p_e \approx 12.5 \). This steady state is achieved by a global balance of oxidation and reduction, and \( H^+ \) ion production and consumption. Above all, the rate of oxidation of reduced S, Fe, and C occurring during the weathering of continental rocks, is balanced by the rate of reduction of higher valent S, Fe, and C into reduced forms during and after deposition onto land and in the sediments.

Oxidation and reduction are accompanied by proton release and proton consumption, respectively. (In order to maintain charge balance, the production of \( e^- \) will eventually be balanced by the production of \( H^+ \).) Furthermore, the dissolution of rocks and the precipitation of minerals are
accompanied by H⁺ consumption and H⁺ release, respectively. Thus, as shown by Broecker (1971), the pe and pH of the surface of our global environment reflect the levels where the oxidation states and the H⁺ ion reservoirs of the weathering sources equal those of the sedimentary products.

1.1 Genesis of Acid Precipitation

The oxidation of carbon, sulfur, and nitrogen, resulting mostly from fossil-fuel burning, disturbs redox conditions in the atmosphere. The atmosphere is more susceptible to anthropogenic emissions than are the terrestrial or aqueous environments, because, from a quantitative point of view, the atmosphere is much smaller than the other reservoirs. Furthermore, the time constants concerning atmospheric alterations are small in comparison with those of the seas and the lithosphere.

In oxidation-reduction reactions, electron transfers (e⁻) are coupled with the transfer of protons (H⁺) to maintain a charge balance. A modification of the redox balance corresponds to a modification of the acid–base balance. The net reactions of the oxidation of C, S, and N exceed reduction reactions in these elemental cycles. A net production of H⁺ ions in atmospheric precipitation is a necessary consequence. The disturbance is transferred to the terrestrial and aquatic environments, and it can impair terrestrial and aquatic ecosystems.

Figure 1 shows the various reactions that involve atmospheric pollutants and natural components in the atmosphere. The following reactions are of particular importance in the formation of acid precipitation: oxidative reactions, either in the gaseous phase or in the aqueous phase, leading to the formation of oxides of C, S, and N (\(\text{CO}_2\), \(\text{SO}_2\), \(\text{SO}_3\), \(\text{H}_2\text{SO}_4\), NO, \(\text{NO}_2\), \(\text{HNO}_2\), and \(\text{HNO}_3\)), absorption of gases into water (cloud droplets, falling raindrops, or fog) and interaction of the resulting acids (\(\text{SO}_2\cdot\text{H}_2\text{O}\), \(\text{H}_2\text{SO}_4\), \(\text{HNO}_3\)) with ammonia (NH₃) and the carbonates of airbore dust, and the scavenging and partial dissolution of aerosols into water. In this case aerosols are produced from the interaction of vapors and airbore (maritime and dust) particles; they often contain (NH₄)₂SO₄ and NH₄NO₃.

The products of the various chemical and physical reactions are eventually returned to the earth’s surface. Usually, one distinguishes between wet and dry deposition. Wet deposition (rainout and washout) includes the flux of all those components that are carried to the earth’s surface by rain or snow, i.e., those dissolved and particulate substances contained in rain or snow. Dry deposition is the flux of particles and gases (especially \(\text{SO}_2\), \(\text{HNO}_3\), and \(\text{NH}_3\)) to the receptor surface during the absence of rain or snow. Deposition also can occur through fog aerosols and droplets, which can be deposited on trees, plants, or the ground. With forests, approximately half of the deposition of \(\text{SO}_4^{2-}\), \(\text{NO}_3^-\), and \(\text{H}^+\) occurs as dry deposition (Lindberg et al. 1986).

We concentrate on three elementary chemical concepts that are the prerequisites to understand the genesis and properties of acid deposition. The first of the three concepts is a simple stoichiometric model, which explains on a mass-balance basis that the composition of rain results primarily from a titration of the acids formed from atmospheric pollutants with the bases (NH₇ and \(\text{CO}_3^{2-}\)-bearing dust particles) introduced into the atmosphere. Next is an illustration of the absorption equilibria of such gases as \(\text{SO}_2\) and NH₃ into water, which represents their interaction with cloud water, raindrops, fog droplets, or surface waters. Finally, a quantitative interpretation of the acid-base balance is presented. This requires a rigorous definition of acid-neutralizing capacity (alkalinity) and base-neutralizing capacity (acidity) to measure the residual acidity of acid precipitation, and to interpret the interaction of acid deposition with the terrestrial and aquatic environment.

1.1.1 Stoichiometric Model

The rainwater shown in Fig. 1 contains an excess of strong acids, most of which originate from the oxidation of sulfur during fossil-fuel combustion, and from the fixation of atmospheric nitrogen to NO and \(\text{NO}_2\) (e.g., during combustion of gasoline by motor vehicles). It also should be mentioned that there are natural sources of acidity, resulting from volcanic activity, from \(\text{H}_2\text{S}\) from anaerobic sediments, and from dimethylsulfide and carbonylsulfide that originate in the ocean. The HCl results from the combustion and decomposition of organochlorine compounds such as polyvinylchloride. Bases originate in the atmo-