SCOPE 51 - Biogeochemistry of Small Catchments

10 Sulphur

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10.1 INTRODUCTION

10.1.1 THE GLOBAL SULPHUR CYCLE AND ITS DISTURBATION BY MAN

The global sulphur cycle is strongly affected by man. Man-made sulphur emissions and acidification have their origin several hundred million years ago when dying plants and, to a much lesser extent, microorganisms and animals were transformed into materials which we today know as fossil fuels-coal, oil and natural gas. Over a couple of hundred years man has rapidly burned a substantial portion of these stores of organic material and released large amounts of sulphur dioxide into the atmosphere.

Current emissions in Europe including the European part of Russia and other CIS countries add up to »20 million tonnes of sulphur (i.e. 40 million tonnes of sulphur dioxide) annually. Large quantities of sulphur dioxide are emitted also in. North America, mostly in the USA, estimated at 15 million tonnes S year^{-1}. Today's worldwide anthropogenic sulphur emissions into the atmosphere total between 70 and 100 million tonnes per year (Rodhe, 1976; Ivanov and Freney, 1983; Galloway and Rodhe, 1991). The atmosphere also contains sulphur supplied by natural emissions (» 60 million tonnes per year; Galloway and Rodhe, 1991). This sulphur also originates from weathering, volcanic emissions, gaseous emissions from soils and oceans, as well as particulates from sea salt and soils. The relative contributions of natural and anthropogenic sources differ widely in different parts of the Earth, depending on the location of pollution sources, especially industry, power plants and highly populated areas. In Northern Europe 10% of atmospheric sulphur is of natural, and 90% of anthropogenic origin. Central Europe and the United Kingdom main sulphur emission source areas are urban and industrial regions.

During the last ten years sulphur emissions in Europe and North America have declined. Some countries have reduced their sulphur emissions by more than 50% (e.g. West Germany and Sweden), while some countries increased emissions during the same period. It is predicted that in the Northern Hemisphere substantial reductions in sulphur emissions will occur by the year 2000.
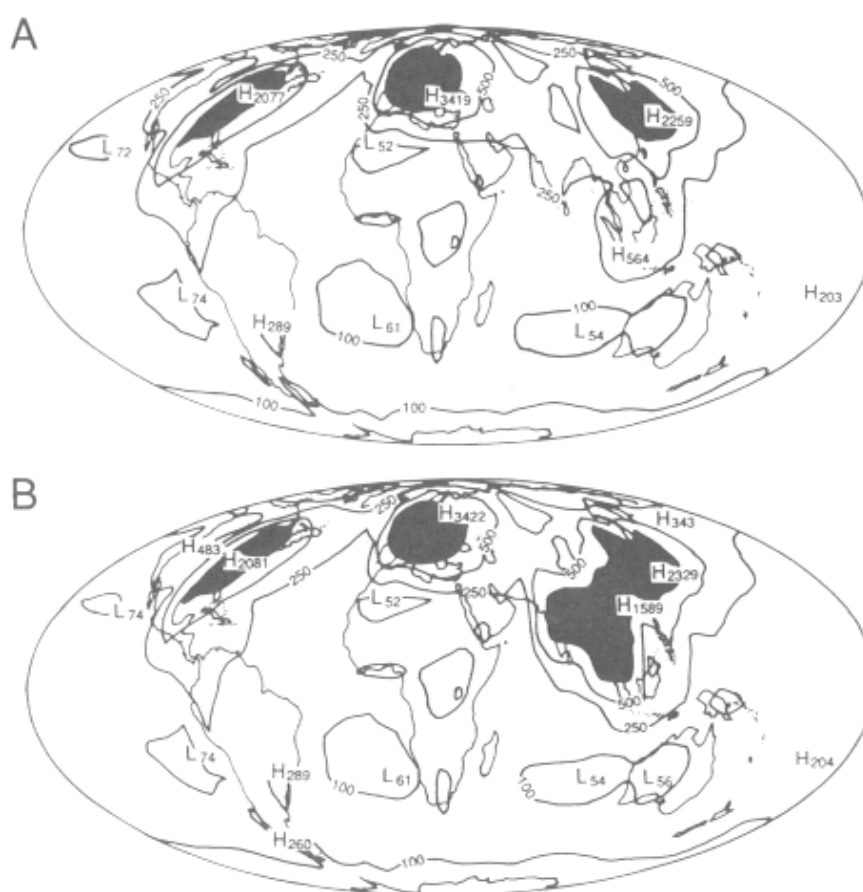

Figure 10.1 (A) Estimated annual total deposition of sulphur resulting from natural (58 Tg S year^{-1}) and anthropogenic (70 Tg S year^{-1}) sources. Units are mg S m^{-2} year^{-1}. (B) Estimated annual deposition of sulphur following an assumed increased emission by 15 Tg S year^{-1} in SE Asia. Other emissions are as in Rodhe *et al.* (1992). "H" and "L" designations refer to the maximum and minimum deposition amounts, respectively (Galloway and Rodhe, 1991; reproduced by permission of the Royal Society of Edinburgh).

However, in large portions of the world, such as China, India, South East Asia, Nigeria, Brazil and other parts of Africa and South America, where population and use of fossil fuels are likely to increase,

regional sulphur pollution may become more of a problem. In these parts of the world ([Figure 10.1](#)) regional sulphur budgets should be constructed and effective assessment should be carried out (Rodhe *et al*., 1988; Galloway and Rodhe, 1991).

10.1.2 SULPHUR IN ECOSYSTEMS

Sulphur emissions from fossil fuel burning are transported over long distances and have been, together with other air pollutants, deposited to aquatic and terrestrial ecosystems. Soot particles from coal burning have been found in dated lake sediments in remote locations of Sweden in layers deposited since the industrial revolution in Europe in the mid-nineteenth century (Renberg and Wik, 1985; Wik *et al*., 1986). After the Second World War and until about 1980, an exponential increase in oil burning occurred in the Northern Hemisphere and the content of soot particles increased dramatically in lake sediments along with acidification of lakes and streams in Norway, Sweden, Scotland, Central Europe and North America (Renberg and Battarbee, 1990; Charles *et al*., 1989; Battarbee *et al*., 1990). Anthropogenic emissions of sulphur and wet and dry deposition of sulphur to ecosystems have followed the same pattern.

For most forest types, storage of sulphur in vegetation represents a small portion, often less than 10% of the total sulphur content in the ecosystem (Mitchell *et al*., 1992b) ([Figure 6.5](#)).

In areas with a small soil pool of sulphur relative to the vegetation compartment, e.g. in Coweeta, USA (Swank and Crossley, 1988), vegetation constitutes a larger fraction (17%) of the total ecosystem pool of sulphur. At coniferous forested sites in Northern Europe, e.g. Gårdsjön in Sweden, the yearly retention of sulphur in the forest stand is less than 2% of the sulphur deposited to the forest. Most of the sulphur input is transported through the catchment (Hultberg, 1985a) because the ecosystem has relatively thin, nutrient-poor soils with low sulphate adsorption capacity of the post-glacial period. This makes a construction of input-output budgets for sulphur a relatively simple task. The sulphur flux leads to extensive chemical and biological changes in lakes and streams (Hultberg and Stenson, 1970; Grahn *et al*., 1974; Almer *et al*., 1974; Hultberg, 1977, 1983, 1985b) and terrestrial ecosystems (Oden, 1968; Likens *et al*., 1977, 1985; Ulrich and Pankrath, 1983; Grodzinski *et al*., 1984; Ulrich, 1984; Matzner 1989).

It is a well-established fact that elevated atmospheric deposition of anthropogenic sulphur combined with lack of retention mechanisms is the main cause why many thousands of lakes and rivers, as well as groundwater systems, have been acidified over large areas in Scandinavia (Hultberg and Wenblad, 1980; Hultberg and Johansson, 1981; Henriksen *et al*., 1988; Bernes, 1991). Sulphur is also the main cause of soil acidification resulting in nutrient losses and possibly forest decline (Paces, 1982; Moldan and Paces, 1987; Reuss and Johnson, 1986; Falkengren-Grerup, 1986; Ulrich, 1984; Tamm and Hallbäcken, 1988; Ashmore *et al*., 1990; Schulze and Freer-Smith, 1991; Hultberg and Likens, 1992).

Integrated research of biological and chemical changes in small catchments is a useful scientific tool to study the biogeochemical cycling of sulphur. Small catchments may also be used for manipulation experiments, important for understanding of processes in affected ecosystems. Such studies have been performed at several sites in Europe and North America during the past decades, but are scarce or non-existent in other parts of the world (Likens *et al*., 1977; Swank and Crossley, 1988; Hultberg *et al*., 1990; Westling and Hultberg, 1990/91; Hultberg and Likens, 1992).

10.1.3 SULPHUR STUDIES IN EUROPE AND NORTH AMERICA

The wet deposition of sulphur has been monitored for almost four decades in northwestern Europe (Granat, 1988; Leck and Rodhe, 1989). Today, wet deposition and atmospheric concentrations of sulphur and other air pollutants are monitored in Europe as part of EMEP programme. Total atmospheric sulphur inputs to forests have been monitored by throughfall chemistry measurements only within specific research projects in each country. Throughfall monitoring in forest plots is, however, currently under way at about 80 sites in Sweden (Ivens *et al*., 1990).

Catchment studies started in North America in the 1930s (Swank and Crossley, 1988) and studies on ecology and biogeochemistry of whole ecosystems including sulphur budgets were initiated in the USA during the early 1960s (Likens *et al*., 1977, 1985) and in the 1970s in Canada (Dillon *et al*., 1982).

Several similar studies were started during the 1960s and 1970s in Europe (Paces, 1982; Ulrich and Pankrath, 1983; Grodzinski *et al*., 1984; Andersson and Olsson, 1985). Input and output fluxes were studied in more than 30 small catchments in Western Europe (Hornung *et al*., 1990) and Eastern Europe (Hauhs *et al*., 1989).

Whole catchment experiments have been used to study effects of increased sulphur inputs on the ecosystem under different forest management practices including harvesting techniques, use of herbicides, changes in vegetation types, ditching, forest road construction, forest fires, fertilizer additions and liming (Likens *et al*., 1970, 1990; Harriman and Morrison, 1982; Swank and Crossley, 1988; Hultberg, 1985a; Hultberg and Grennfelt, 1986, 1992). Experimental additions and reductions of sulphur inputs to catchments are part of research projects currently in progress in Norway and Sweden (Wright *et al*., 1988; Wright, 1989; Wright and Henriksen 1990; Hultberg *et al*., 1990; Hultberg and Grennfelt, 1992; Hultberg and Likens, 1992).

Measurements of natural stable isotope ratios (^{34}S/^{32}S) in small catchments can be a powerful tool for studying sulphur in deposition, vegetation, soils, soil water and runoff in forested catchments. These measurements are part of research projects under way in western Germany (Giesemann *et al*., personal communication), Sweden (C-M.Mört *et al*., personal communication, Stockholm University) as well as the United States at Hubbard Brook Experimental Forest, NH (Fuller *et al*., 1987) and Bear Brook Watershed, Maine (Stam *et al*., 1992). ^{35}S labelling has been used to quantify the atmospheric uptake of sulphur dioxide relative to root uptake and subsequent release of sulphate by throughfall and stemflow from coniferous and deciduous tree species (Garten *et al*., 1988; Lindberg and Garten, 1988; Garten, 1990).

Mass balance studies and experiments in small catchments together with monitoring of wet deposition, throughfall and runoff, have been used to quantify sulphur inputs by dry deposition (Hultberg; 1985a; Likens *et al*., 1990; Hultberg and Grennfelt, 1992; Hultberg and Likens, 1992).

10.2 ATMOSPHERIC INPUT TO CATCHMENTS

10.2.1 CHEMICAL FORMS AND MECHANISMS OF DEPOSITION

Sulphur in the atmosphere generally occurs in three main chemical forms, either in the gas phase as SO_2, as particulate SO_4^{2-}, or in the ionic form as SO_4^{2-} dissolved in water. The emissions from both anthropogenic and natural sources are dominated by SO_2 and it is generally accepted that the transformation to SO_4^{2-} is controlled by the supply of oxidants such as H_2O_2 and OH^- radicals. Most of the SO_4^{2-} is dissolved as sulphuric acid in water and deposited by precipitation. Some of the acidity may be neutralized by NH_3 which forms particulates in the atmosphere and/or dissolves in the water phase in clouds or fog.

Sulphur also occurs as coarse particles, such as sea-derived aerosol and as particles of calcium and magnesium sulphates formed after a reaction of SO_2 with soil particles in the atmosphere. An important reaction in forested catchments is the uptake in stomata and oxidation of SO_2 to SO_4^{2-} inside needles and leaves. Chemical reactions also occur on vegetation surfaces and SO_2 deposition is enhanced in the presence of NH_3 (co-deposition) (Heil and Diemont, 1983; van Hove *et al*., 1989; Ivens, 1990; Ivens *et al*., 1990; Fowler *et al*., 1991).

Quantification of the total sulphur input via deposition at the catchment level is critical in most studies of biogeochemical cycling of sulphur. As discussed in Chapter 3, three processes are involved; wet deposition by precipitation; dry deposition from surface air masses; and, at some locations, direct deposition of droplets from fog and cloud impinging on to ground vegetation and forests in mountainous areas.

The relative importance of these processes varies greatly among different catchments, as does the total

amount of sulphur deposited. Thus, deposition rates vary from 1 to 2 kg ha^{-1} year^{-1} in remote regions to more than 120 kg ha^{-1} year^{-1} in polluted areas (Figure 10.2) (Paces, 1985; Hultberg, 1983; Hultberg and Grennfelt, 1986; Hauhs *et al.,* 1989; Ivens *et al.*, 1990; Hultberg and Likens, 1992).

Over large areas in Europe and North America a large proportion of the sulphur input is made up of gaseous SO_2, which is efficiently scavenged by forests as dry deposition. Wet deposition is limited by solubility and oxidation in clouds and precipitation, and sulphur deposition by precipitation in urban areas is not significantly greater than in the rural surrounding regions. Thus in forested catchments in polluted areas normally a greater proportion of the deposition is made up by dry deposition (Figure 10.3). This became apparent when a range of catchments in different pollution climates were compared (Hultberg, 1983).

At more remote sites a greater proportion of SO_2 is converted to particulate sulphate, which is much less readily deposited in dry conditions, but is efficiently incorporated in cloud droplets and scavenged by precipitation. The oxidation of SO_2 to the SO_4^{2-} aerosol takes place partly by gaseous photochemical processes forming sub-micron particles. The typical conversion rate is 1 to 2% per hour in daytime conditions, subsequently reacting with available NH_3. It also takes place in clouds where oxidation rates can be highly variable depending on the availability of H_2O_2, which is consumed rapidly and independently of cloud water pH and O_3 concentrations. In some polluted regions catalytic oxidation in clouds may also be induced by high levels of Fe or Mn (Brosset, 1978). The acidity associated with the sulphur input from aged air and its magnitude will thus depend on its origin and history.
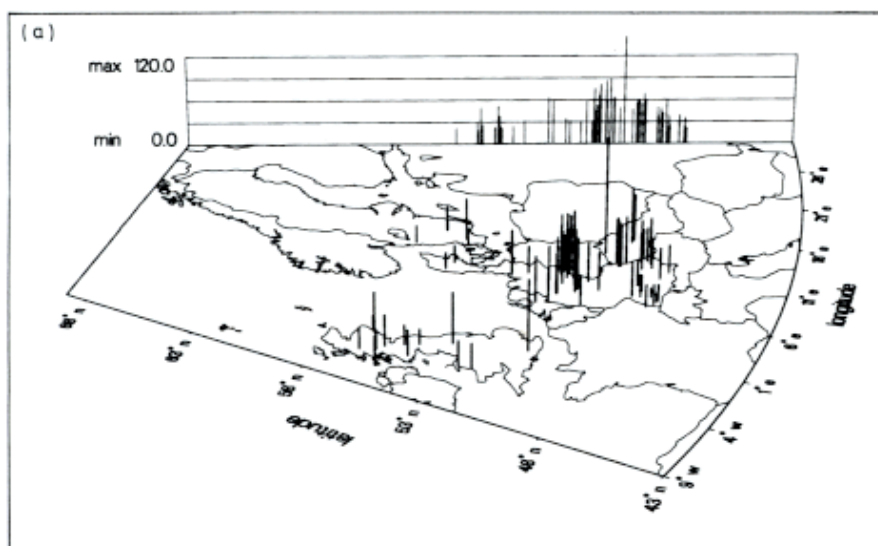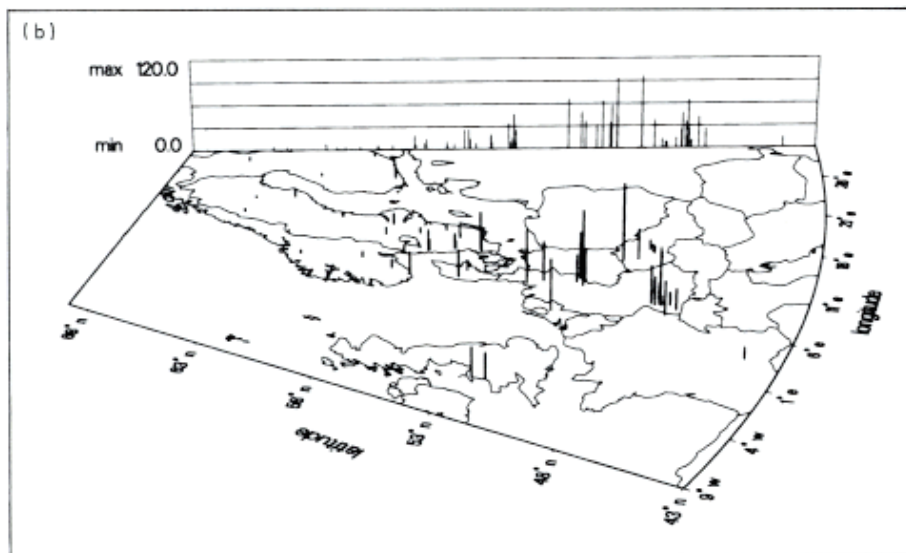
Figure 10.2 (a) Sulphur throughfall fluxes (kg S ha^{-1}) in coniferous forest stands (mainly Norway spruce). (b) Sulphur output by runoff and/or seepage from forested catchments (Hauhs *et al*., 1989; reproduced by permission of M. Hauhs). Values are seasalt corrected, e.g. marine aerosol contribution was subtracted.
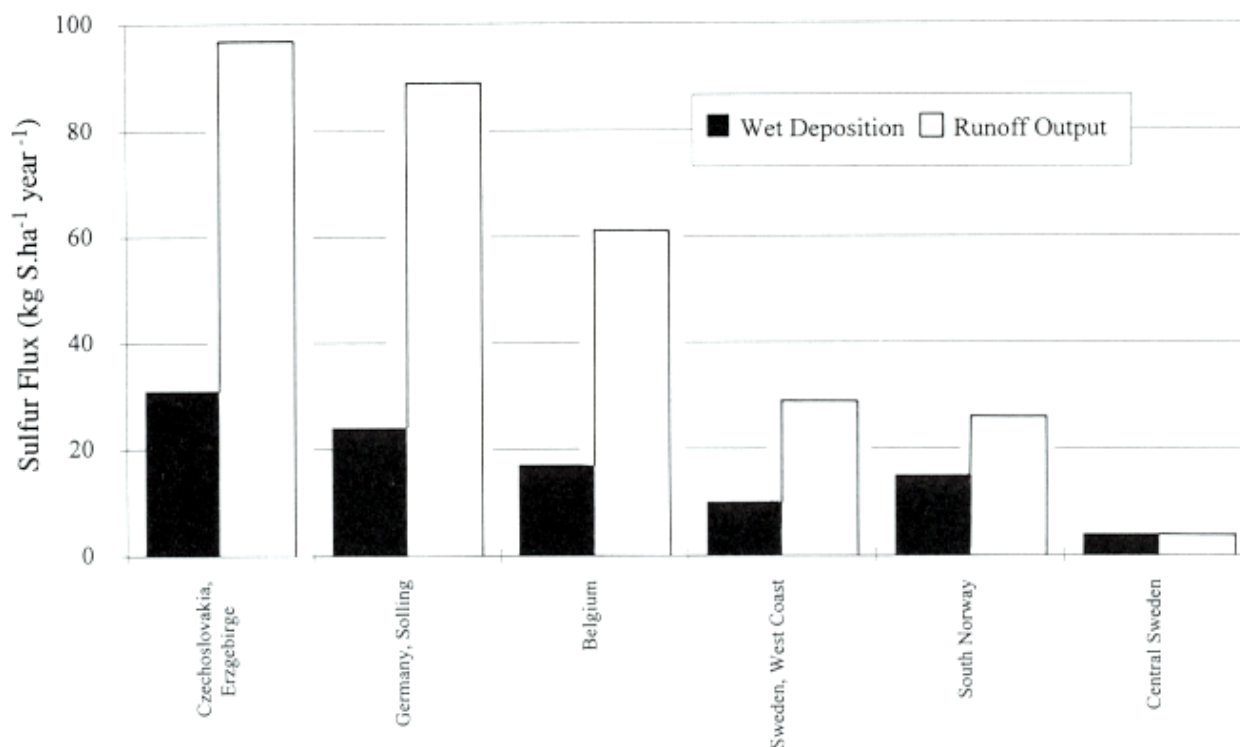
Figure10.3 Sulphur output by runoff and wet deposition from six coniferous forested catchments in Central Europe, Sweden and Norway (from Hultberg, 1983). Data are taken from Paces (1983) for Czechoslovakia, from Matzner *et al*. (1982) for Germany, from Buldgen and Remacle (1984) for Belgium, from Hultberg (1985) for Swedish West Coast, from Wright and Johannesen (1980) for Norway and from Rosén (1982) for Central Sweden.

10.2.2 QUANTIFICATION OF SULPHUR DEPOSITION

Although input of sulphur by precipitation has been monitored in every catchment study focusing on biogeochemistry of sulphur, only a limited number of investigations have considered the contribution of

dry and cloud deposition. If only wet deposition is considered, the total sulphur input may be largely underestimated. This will especially be the case with sulphur inputs to forested catchments with high frequencies of fog and clouds and to catchments close to source areas.

As mentioned in Chapter 3, two methods have been mainly used to quantify the dry and cloud deposition: model calculations and throughfall measurements. Recently it has been shown that runoff monitoring may be used in areas with no or negligible sulphur retention in the soils. Since these methods are indirect it is important to verify them by independent measurements. A number of such validations have been published (Hultberg, 1983, 1985a; Hultberg and Grennfelt, 1986, 1992; Likens *et al.*, 1990; Hultberg and Likens, 1992) showing that throughfall plus stemflow and runoff measurements are satisfactory in most cases.

Lindberg and Garten (1988), Garten (1990) and Cape *et al.* (1992) showed that application of ^{35}S to soils resulted only in a minor uptake and internal leaching (3% and 4%, respectively) from coniferous and deciduous canopies. They also concluded that throughfall plus stemflow measurements can be used to quantify total sulphur deposition to forests. These methods have been used during the Integrated Forest Study (IFS), in which forest plots in the USA, Canada and Norway were included. The fluxes showed large spatial variability, yet across all IFS sites fluxes of total sulphur deposition, estimated by modelling and throughfall plus stemflow measurements, were strongly related suggesting that uptake and leaching are small relative to the total sulphur deposition to the tree canopies (Johnson and Lindberg, 1992). The overall lack of canopy interactions with sulphur makes throughfall plus stemflow measurements an excellent tool for quantifying atmospheric sulphur deposition to forested catchments. Other studies support these findings (Mayer and Ulrich, 1974; Hultberg, 1985a; Lindberg *et al.*, 1986). Results from Hubbard Brook in the USA does not support such conclusions, but at this site mass balance studies of sulphur show that runoff can be used in the estimates of dry deposition of sulphur (Likens *et al.*, 1990). The limitation of this method is that the runoff flux of sulphur can only be used to estimate dry plus cloud deposition in areas where precipitation inputs are known and where biomass retention, soil retention and weathering release of sulphur from the soils are low.

Model calculations now are sophisticated enough to produce reasonably good estimates of dry and cloud deposition at least to a number of well-defined receptors (Lindberg *et al.*, 1990; Fowler *et al.*, 1991). Monitoring of SO_2 and SO_4^{2-} particulate concentrations, as well as wet deposition, fog and cloud concentrations and meteorological data, is necessary in order to model the total sulphur deposition to forested ecosystems. This approach is, however, very expensive and insufficiently tested compared to monitoring by throughfall plus stemflow.

10.2.3 FACTORS INFLUENCING SULPHUR DEPOSITION

The input of sulphur by dry deposition and cloud interception may vary considerably depending on the topography of the catchment, the elevation above the sea level, type of vegetation, occurrence of forest edges and presence or absence of farming sources of NH_3 (Grennfelt *et al.*, 1985; Grennfelt and Hultberg, 1986; Hasselroth and Grennfelt, 1987; Ivens *et al.*, 1990; Fowler *et al.*, 1991).

The forest cover enhances the total sulphur deposition especially in the case of coniferous forests. A total increase relative to open field deposition by 100 to 500% in south Scandinavia and Northern/Central Europe due to dry and fog/cloud deposition was observed (Hultberg, 1983; Ivens *et al.,* 1990; Hauhs *et al.*, 1989; Fowler *et at.,* 1991; Hultberg and Likens, 1992). A linear relationship between sulphur export in runoff and the percentage of coniferous forest cover (Figure 10.4) was shown to exist for different catchments in the Lake Gårdsjön area (Hultberg, 1985a). Forest edges may locally increase sulphur deposition by 50% to 200% although the edge effect may not lead to a significant increase in the total deposition to the catchment. Edge effects should, however, be considered, for example in the establishment of sampling strategy for throughfall monitoring (Grennfelt and Hultberg, 1986; Hasselroth and Grennfelt, 1987; Ivens 1990).
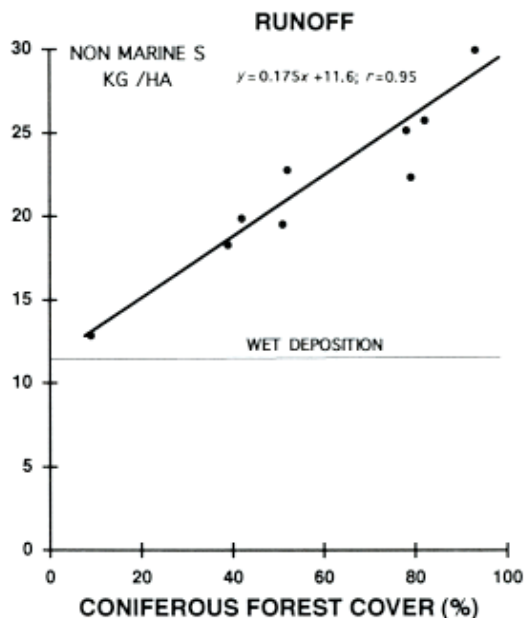
Figure 10.4 Sulphur output from terrestrial catchments (kg S ha^{-1} year^{-1}) vs. coniferous forest cover of the catchment area (from Hultberg and Likens, 1992).

Deposition of sulphate aerosol may be sharply enhanced over upper slopes by the "feeder-seeder" mechanism. In this situation, as air is advected above the condensation level over highland, the aerosols act as condensation nuclei for cloud droplets in the new "feeder cloud", and are then very efficiently scavenged by precipitation falling from overlying "seeder cloud". For example, over Great Dunn Fell in the United Kingdom concentrations of sulphate ions in precipitation have been found to increase by a factor of 2-3 over the altitude range 200 to 850 metres, with an accompanying increase in precipitation amount of approximately 200% (Figure 10.5). It means that deposition of SO$_4^{2-}$ increases by 400 to 600% over this altitude range. This could be a complication in studies of steep-sided catchments, inducing considerable variation in sulphur deposition up the slopes (*Fowler et al., 1991*).
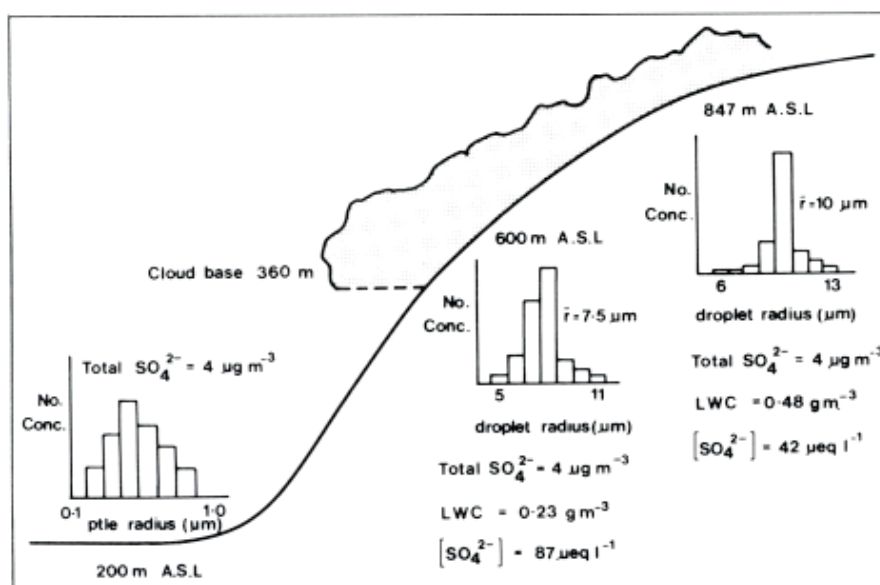

Figure 10.5 Example of changes in particle size and ionic concentrations as aerosols are activated into cloud droplets and grow as they are advected up a hill slope (from Fowler *et al*., 1991; reproduced by permission of D. Fowler and The Royal Society of Edinburgh).

Direct deposition from clouds also increases systematically with altitude and the associated higher incidence of cloud cover, which also varies systematically with season, time of the day and meteorological situation. Deposition of cloud droplets of the order of 10 μm in radius takes place at a similar rate to the downward transfer of momentum, and hence is enhanced by higher wind speed and channelling effects, and by greater surface roughness. Field studies have confirmed that vegetation is an efficient scavenger for deposition of cloud droplets, with effective deposition velocities equivalent to 1 to 4 cm S^{-1} over moorlands, to values in excess of 10 cm S^{-1} over forests (Fowler *et al*., 1988). Cloud chemistry can be very important, with high entrainment of H_2O_2 in oxidant-rich air forming very acidic clouds, or local ammonia sources from livestock farming or alkaline fly-ash input enhancing the uptake and oxidation of SO_2. Thus in some cases sulphur concentrations in cloud droplets may be very high.

The contribution of direct deposition of sulphur from cloud droplets has been quantified and theoretical estimates indicate its importance in upland catchments (Fowler *et al*., 1991). For example, up to 75% of the sulphur deposition has been attributed to direct deposition from clouds measured at a high-altitude site in Quebec, Canada. Calculated estimates of the relative contributions of direct cloud deposition averaged over different altitude bands over the Grampian Mountains of Scotland (ApSimon *et al*., 1990) show that direct deposition from clouds is expected to exceed dry deposition above about 500 metres a.s.l.

10.2.4 REGIONAL DRY DEPOSITION

Dry deposition of sulphur has been estimated for a number of individual small catchments, where frequent measurements of wet deposition, throughfall and catchment output are available. The procedure assumes that the catchment is at steady state in respect to sulphur and dry deposition equals net release, calculated from the difference of measured atmospheric deposition and streamwater export (Hultberg, 1985a; Likens *et al*., 1990; Hultberg and Grennfelt, 1992; Hultberg and Likens, 1992).

It has been possible to calculate dry deposition for a larger set of sites in a region, using sparse but more geographically extensive data sets. For the state of Maine in the northeastern USA, Norton *et al*. (1988) combined a variety of lake survey data on sulphate concentration with regional wet deposition data and estimates of evapotranspiration, and found that additional sources of sulphur were required to explain lake sulphate concentrations for this area. These additional sources of sulphur were likely to be dry and cloud deposition. Church *et al*. (1989) have performed a similar analysis for the entire northeastern USA above the limit of the last continental glaciation. This analysis used uniform data sets on water chemistry, wet deposition and runoff. A general decrease in dry deposition from the southwest to the northeast (consistent with the national pattern of SO_2 emissions, as well as with local SO_2 sources) was shown by this analysis. The regional ratio of dry to wet deposition of approximately 0.4 to 0.5 was in agreement with estimates at more intensively studied sites in the region. Sub-regional patterns were also consistent with estimates of sulphur deposition provided by the Regional Acid Deposition Model (RADM).

Such regional analyses support data from more localized intensive small catchment studies. They have a drawback, however, that large internally consistent regional data sets are available only for one or two years. Watershed retention of sulphur can be at a quasi-steady state in the long run but still have marked annual variability during exceptionally wet or dry years.

10.3 CYCLING IN SOILS

10.3.1 ADSORPTION/DESORPTION IN SOILS

Catchment studies have clearly demonstrated that soil processes in the forest floor and the mineral soil play a significant role in regulating sulphate flux. For example, Rochelle *et al*. (1987) in examining input-output budgets for catchments in North America found a positive correlation between the degree of soil weathering and net retention of sulphate. Such findings support conclusions of laboratory studies (Harrison *et al*., 1989) which have found that highly weathered soils generally have higher sulphate adsorption capacities than less weathered soils.

There is a close relationship between low sulphate adsorption of soils and acidification of surface waters in catchments with elevated atmospheric deposition. Therefore in regions such as southeastern Canada, the northwestern USA and Europe (especially Scandinavia), which are characterized by soils with low sulphate adsorption, sulphate inputs from atmospheric deposition are closely balanced by sulphate outputs through streamwater (Hultberg, 1985a; Likens *et al*., 1990; NAPAP 1990; Hultberg and Grennfelt, 1992).

Such balances, however, are not characteristic of all catchments. For example at Coweeta in North Carolina (USA), there exists a strong net retention in a mixed hardwood catchment. Plot and laboratory experiments suggest that microbial immobilization processes may significantly contribute to sulphur retention (Swank and Crossley, 1988). To determine the relative importance of abiotic (adsorption/desorption) and biotic (immobilization/mineralization) processes in regulating retention or loss, studies using techniques such as radioactive isotopes (^{35}S) or stable isotopes (^{34}S/^{32}S) are also required (David *et al*., 1984; Fuller *et al*., 1987).

10.3.2 BIOMASS ACCUMULATION

The vegetation pool even in forest ecosystems represents less than 10% of the total ecosystem content of sulphur since the forest floor and especially the mineral soil serve as the major reservoirs of this element (Johnson, 1984; Mitchell *et al.,* 1992a). Furthermore, the cycling through vegetation, as reflected in litterfall, is generally small compared to other fluxes, such as total deposition or throughfall, for most forest ecosystems. This is due to the relatively low nutrient demand for sulphur compared with other elements such as nitrogen and calcium (Johnson *et al*., 1985). It appears that vegetation plays only a limited direct role in regulating sulphur flux in forests except in some regions of Australia and western North America which have low anthropogenically derived input coupled with sulphur deficient soils (Turner and Lambert, 1980).

10.3.3 GASEOUS EMISSIONS

Quantification of catchment sulphur budget may also be helpful in evaluating the importance of gaseous emissions both with respect to ecosystem balances and the contribution of terrestrial emissions to the global sulphur cycle (Haines, 1991). For example, it has been suggested that volatilization, which may be especially important for some tropical plants, may be a major factor in explaining discrepancies in the sulphur budgets of tropical systems (Haines *et al.,* 1983). Analysis of catchment budgets of tropical forests, for which presently no data are available, may provide an important insight into this question. However, such studies will have to be done on sites without high sulphate adsorption capacities; such sites may be difficult to find in tropical areas since the soils are typically highly weathered.

Gaseous emissions of H$_2$S and other reduced sulphur compounds occur from wetlands and tree canopies from forested catchments in Northern Europe but no quantitative data are available (Hällgren *et al*., 1982).

In catchments containing *Sphagnum-dominated* wetlands, studies of sulphur gaseous production and release have recently started in the USA (B. Haines, personal communication) and Sweden. Gaseous emissions of hydrogen sulphide, methyl mercaptan and dimethyl sulphide (DMS) are measured and catchments experimental manipulations (liming, N-fertilization, sulphur additions and roof) will be used.

10.3.4 LEACHING OF NUTRIENTS

One of the most important effects of sulphur deposition is extensive acidification and leaching of nutrients that have occurred in forest soils during the last 50 to 100 years in Northern/Central Europe and possibly in parts of North America (Paces, 1982; Tamm and Hallbäcken, 1988; Reuss and Johnson 1986; Schulze and Freer-Smith, 1991; Hultberg and Likens, 1992). The loss of base cations like calcium, magnesium and potassium may be causing malnutrition to coniferous and hardwood forests over large regions of Europe. The loss of base cations was shown to be quantitatively related to the speciation of the cation deposited together with the sulphate, where H$^+$ and/or NH$_4^+$ together with the leaching of sulphate cause a concomitant release of either basic nutrients (Ca^{2+}, Mg^{2+}, K$^+$) or toxic acidic (H$^+$,

Al^{3+}) cations. Experimental additions within SWAP (Surface Waters Acidification Programme) at Lake Gårdsjön showed that about 40% of the acid sulphate input resulted in base cation loss and 60% in leaching of the toxic acidic cations H^+ and Al^{3+} (Hultberg *et al*., 1990). Increased concentrations of Al^{3+} cause higher retention of phosphorus which precipitates in the mineral soils and becomes less available for root uptake. Consequently, foliar analyses have shown Ca, Mg, K and P malnutrition in forests experiencing signs of decline (Ulrich, 1984; Ashmore *et al*., 1990; Schulze and Freer-Smith, 1991).

The reversibility of sulphate adsorption and its prediction (Harrison *et al*., 1989: Mitchell *et al*., 1992a) plays an important role in forecasting recovery of ecosystems following a decrease in emissions. If sulphate adsorption is completely reversible, decrease in loadings and hence lowering sulphate concentration in the soil solution will cause previously adsorbed sulphur to be released. Under such conditions water quality improvement will be delayed until a new equilibrium level of adsorbed sulphate is reached. Such pattern of sulphur behaviour has been generally assumed in simulation models (Mitchell *et al*., 1992a). In contrast, if sulphate is irreversibly held, a decrease in deposition will cause rapid decrease in sulphate concentrations in soil solutions and surface waters. Hence water quality improvement will also occur fast.

10.4 ACIDIFICATION

10.4.1 CRITICAL LOADS

Critical loads were introduced in 1988 by the UNECE Convention on Long Range Transboundary Air Pollution as a tool for the development of abatement strategies and international agreements on reduction of regional air pollutants, which cause acidification in forest soils and surface waters (e.g. sulphur) and eutrophication in terrestrial ecosystems, freshwaters and marine waters (e.g. nitrogen).

The critical load was defined as:

A quantitative estimate of an exposure to one or more pollutants below which significant harmful effects on specified sensitive elements of the environment do not occur according to present knowledge

(Nilsson and Grennfelt, 1988)

The critical-load approach is based on the assumption that a pollution load exists below which no harmful effects occur. The critical load concept is visualized in Figure 10.6. Based on the knowledge of the present load and the critical load, the reduction in pollution load may be calculated. The term target load in Figure 10.6 illustrates an administrative use of the critical load; if the target load is chosen above the critical load it is expected that some areas will still be damaged; if the target load is chosen below the critical load a safety factor is included.

The UN ECE critical load concept was developed for acidification and for eutrophication by nitrogen. The critical load for acidification is defined as:
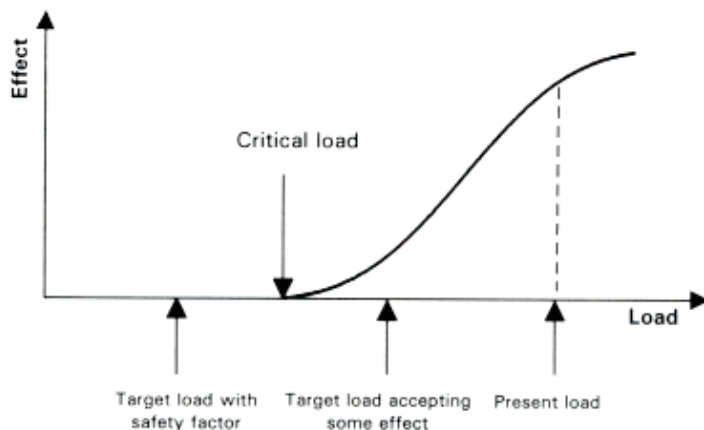
Figure 10.6 Illustration of the critical load and target load concepts (see text for explanations).

> The highest deposition of acidifying compounds that will not cause chemical changes leading to long-term harmful effects on ecosystem structure and function
>
> (Nilsson and Grennfelt. 1988)

The definition requires further definitions of what is meant by harmful effects and also how these effects are linked to chemical criteria in different compartments of an ecosystem. Critical loads have so far been studied mainly in connection with forest soils. groundwater and surface waters acidification. A number of different methods for the determination of critical loads have been developed (Nilsson and Grennfelt. l988; Sverdrup *et al*., 1990; Hettelingh *et al*., 1991) and these methods can be used to map the areas (Hettelingh *et al*., 1991) where critical loads are being exceeded. and by comparing the level of excess with the deposition the necessary reduction to meet the critical load can be estimated (Aaman *et al*., 1991).

The methods developed for calculating a theoretical load to forest soils can be divided into two groups static and dynamic. By the dynamic method episodes and the development of the chemical status of the ecosystem can be forecasted under different scenarios for atmospheric inputs. The static method remains the crucial concept for critical load determination and will be discussed further.

As a first approach. a rough estimate may be derived from a simple analysis of soil properties. Such a set of critical loads for acidification is given in Table 10.1 (Nilsson and Grennfelt. 1988).

The static approach can be further developed including quantitative data on dif ferent flows and processes influencing the acidification of the soil. In the manual (Hettelingh *et al*.. 199l) developed for the mapping of critical loads within the UN ECE region. the critical load (CL_{acidif} for acidification of a forest ecosystem was determined by the following equation:

Table 10.1 Critical loads for the acidification of forest soils as derived at the UN ECE workshop in Skokloster 1988 (Nilsson and Grennfelt, 1988)

Class	Minerals controlling weathering	Usual parent rock	Total acidity (kmol H^+) (km^{-2} year^{-1})	Equivalent amount of sulphur (kg ha^{-1} year^{-1})
1	Quartz K-feldspar	Granite Quartzite	<20	<3
2	Muscovite Plagioclase Biotite	Granite Gneiss	20. 50	3. 8

2	(<5%)	Granite Gneiss	20-50	5-8
3	Biotite Amphibole (< 5%)	Granodiorite Greywacke Schist Gabbro	50-100	8-16
4	Pyroxene Epidote Olivine (<5%)	Gabbro Basalt	100-200	16-32
5	Carbonates Marlstone	Limestone	<200	<32

$$CL_{acidif} = BC_{weathering} + BC_{leaching} - BC_{tree\ accumulation} - AC_{N\text{-}transformations} \qquad (10.1)$$

where BC stands for the flows of base cations and AC for acidity input. The term critical load for acidification may be expressed as:

$$CL_{acidif} = SO_{x\ dep} + NO_{xdep} - BC_{dep} \qquad (10.2)$$

where BC_{dep} includes the deposition of ammonium.

Based on these equations it is obvious that it is possible to quantify the critical load for sulphur only when taking into account the input of base cations and different nitrogen species and the internal conversions of nitrogen.

For a development of European abatement strategies the critical loads and present deposition have to be mapped. Existing monitoring of atmospheric deposition has to be linked with the maps of critical loads to promote development of regional air pollution source-receptor models. Application of the critical loads concept in small catchments which are homogeneous in terms of soil composition and land-use offers a very good field site for a thorough examination of the critical loads concept and its underlying assumptions.

10.4.2 MODELLING SOILS AND STREAMWATER CHEMISTRY

Modelling the effects of sulphur deposition on water quality is facilitated by a number of catchment-scale models (e.g. SAFE, MAGIC, Birkenes, ILWAS). Interest exists in modelling for better understanding of sulphur cycling in soils and forecasting changes in soil and surface water chemistry. Modelling is best undertaken at the small catchment level where soil variability is known and monitoring of outputs is possible.

Currently, sulphur cycling and transport in models of small catchments are represented as inorganic sulphate adsorption (Gherini *et al.,* 1985; Cosby *et al.* 1986; Schnoor, 1984; Mitchell and Fuller, 1988), described as simple partitioning or adsorption isotherms. In all the cases, adsorption is modelled as being completely reversible.

It is clear that in many soils, the pool of organically bound sulphur (either as carbon-bonded sulphur or as ester sulphate) is much larger than the inorganic adsorbed pool. The transfer rates between various forms of organic sulphur or between the total organic pool and inorganic pool are, however, virtually unknown. Results from some small catchment studies (Hultberg, 1983, 1985a; Hultberg and Grennfelt, 1986, 1992; Likens *et al.,* 1990) indicate that net change in size of the organic pool may be relatively small over periods of up to 10 to 20 years.

Existing long-term projections of the effects of sulphur deposition on s water chemistry suffer from the lack of knowledge. The longer the time scale projections, the greater is the uncertainty (Church, 1989). Existing projections correspond reasonably well to stream chemistry observations for a few systems in

the USA (Church *et al.,* 1990). Due to the relatively short duration (5-10 years) of most observations, the question remains concerning projections over longer perid of time.

10.4.3 LONG-TERM STUDIES

 Importance of long-term studies of the sulphur cycle can be exemplified by ten-year estimates of dry deposition based on monitoring of through fall and runoff at for the Gårdsjön watershed (Hultberg and Grennfelt, 1992). The study shows that although 10 year mean sulphur dry deposition estimates were very similar, among the individual years there were large differences between the two methods (Figure 10.7) mainly depending on differences in hydrology between years. Similarresults on sulphur deposition were obtained by the 23-year study of runoff and wet deposition in the Hubbard Brook catchment (Figure 10.8) (Likens *et al.,* 1990).

The estimated dry deposition from these long-term studies of runoff and throughfall corresponds well with the estimates of dry deposition based on model calculations from the monitored SO_2 and particulate SO_4^{2-} concentrations. Dry years may give low output of sulphur from the soil, and wet years a corresponding high release of sulphur (Hultberg and Likens, 1992). Even processes in the tree canopy such as uptake and release of SO_2 may retard sulphur transport through the catchments. Average values over a number of years strongly show the importance of long-term monitoring for understanding of the biogeochemistry of sulphur

Long-term studies in catchments exposed to enhanced dry deposition of SO_2 from the brown-coal burning in northwest Czechoslovakia started at the onset of forest decline in Krusne hory Mountains (Paces, 1982, 1985; Moldan, 1991). These studies show that severe chemical changes have occurred in surface water as well as on the total mass balance of base cations and other ecosystem functions (Paces, 1982; Moldan and Paces, 1987; Cerný, 1992). The forest decline that followed in the catchments later resulted in a decrease in sulphur export, presumably due to decreased dry deposition of SO_2 in the absence of well-developed canopies (Cerný, in press).
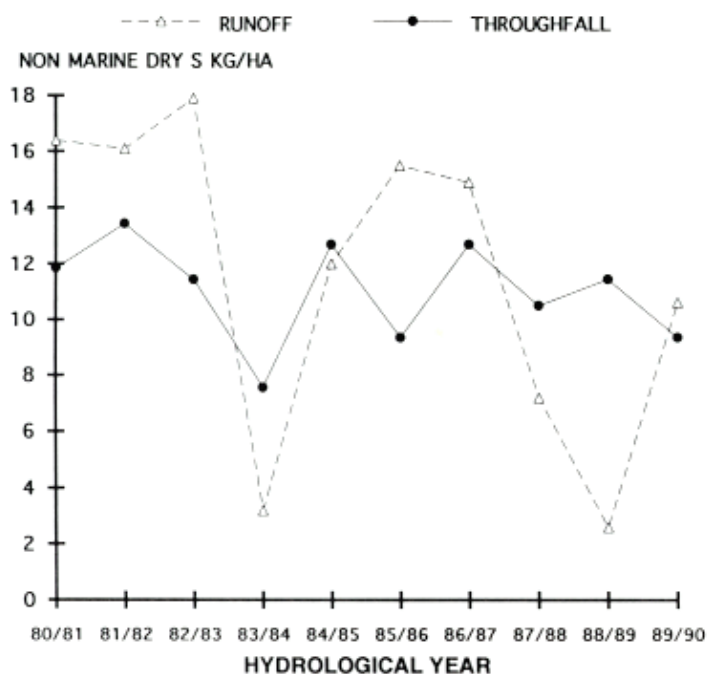

Figure 10.7 Dry deposition of sulphur estimated from throughfall+stemflow and runoff minus wet deposition, respectively, from a catchment at Gårdsjön in SW Sweden (from Hultberg and Likens, 1992).

10.5 WHOLE ECOSYSTEM MANIPULATIONS

Experimental manipulations of catchments provide an insight into factors regulating sulphur flux through the soil. For example, sulphur additions to catchments in Sweden (Hultberg *et al.*, 1990) have confirmed that these soils have small retention capacity and that sulphate was transported through the catchment at the same speed as water. It has also been shown for hardwood forests in the northeastern USA, that tree removal by either clearcutting or whole-tree harvesting has a major impact on sulphur losses (Nodvin *et al.*, 1988). For example a whole-tree harvest of a catchment at Hubbard Brook resulted in a decreased sulphate loss via soil leaching and streamflow. It was suggested that this decrease was directly attributable to an enhanced sulphate adsorption. After tree removal there was an acceleration in nitrification and concomitant generation of H^+, the latter depressing the soil pH and increasing the sulphate adsorption potential (Mitchell *et al.*, 1989; Likens *et al.*, 1990). Clearcutting of a coniferous forest in a catchment at Lake Gårdsjön in Sweden also led to a decrease in sulphate flux but also a decrease in H^+ concentration. It was suggested that this decrease was due to lower dry deposition inputs and that no changes occurred in sulphate adsorption in the soil (Hultberg and Grennfelt, 1992). For both the Hubbard Brook and Lake Gårdsjön experiments, different interpretations of the results were supported by ancillary experiments (Nodvin *et al.*, 1988; Hultberg *et al.*, 1990).
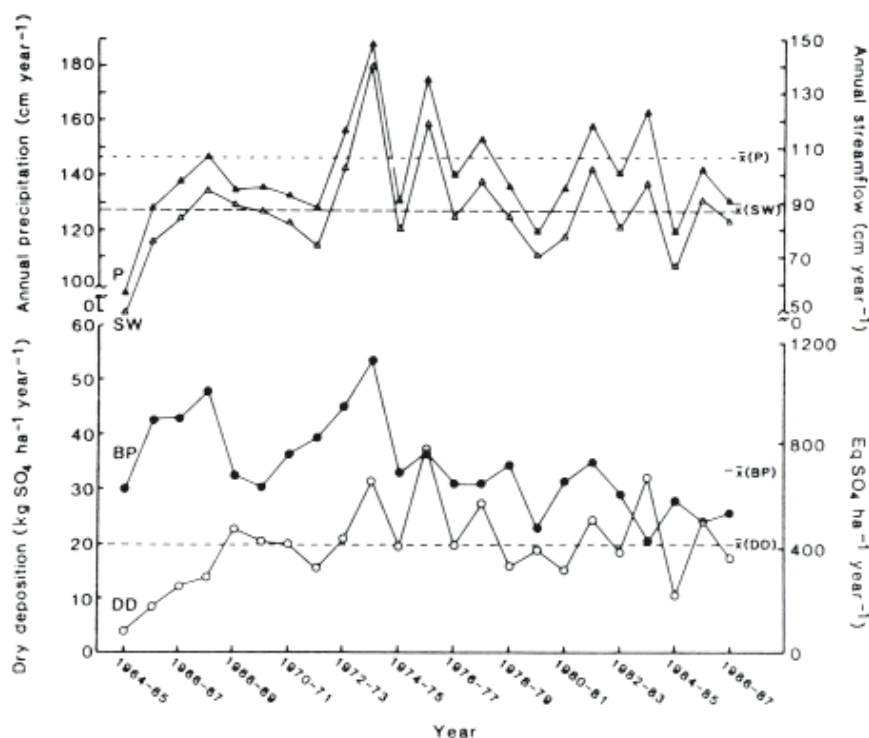

Figure 10.8 Annual precipitation (P), streamflow (SW), wet bulk deposition (BP) and dry deposition (DD) of SO_4^{2-} for watershed 6 of the Hubbard Brook Experimental Forest during 1964-65 through 1986-87 (from Likens *et al.*, 1990; reproduced by permission of Munksgaard International Publishers Ltd).

Monitoring sulphate fluxes in catchments which show decreasing atmospheric inputs, as has been demonstrated for the northeastern USA (Likens *et al.*, 1990), is important for elucidation of reversibility. An experimental study on reversibility of sulphate-related acidification of a small catchment (800 m^2) covered by a transparent roof has been under way since June 1984 in southernmost Norway and sulphur output has shown a general decline by 50% after 3.5 years, beginning five months after the onset of the treatment (Wright *et al.*, 1988; Wright, 1989; Wright and Henriksen, 1990). A similar roof experiment in a 6500 m^2 catchment with 80- to 90-year-old Norway spruce (350 trees) and podzolic soils at the Gårdsjön watershed was initiated in April 1991 (Hultberg *et al.*, 1993).

Experimental manipulations by means of increasing or decreasing sulphur inputs to small catchments performed in concert with modelling activities are currently under way in Norway, Sweden, Denmark and the USA. These studies will be crucial for expanding our knowledge of the effects of sulphur deposition and in adding faith to model projections.

10.6 SUMMARY AND RESEARCH RECOMMENDATIONS

The above sections have shown that catchment studies can contribute very effectively to our understanding of the biogeochemical cycling of sulphur. In particular they can provide estimates of dry and fog/cloud deposition as well as wet deposition, and describe the variations due to catchment topography. It has been pointed out that variations in tree cover or large changes in altitude inside catchments can make significant differences in sulphur inputs, a factor which needs to be recognized in planning throughfall and precipitation measurements. The importance of catchment studies in understanding the uptake, retention and release of sulphur by runoff has also been illustrated. Because of changes among dry and wet years, and consequent deviation from equilibrium conditions, the need for long-term studies is emphasized.

Illustrations have also been provided of catchments in which inputs of sulphur have been significantly reduced, for example by decreased emissions to the atmosphere, tree felling and installation of a roof. This provides an excellent opportunity for studying the response of the catchment and to establish important information on the reversibility of high sulphate loadings in soils and on rates of recovery.

Important aspects of the biogeochemical cycling of sulphur have been learnt from small catchment studies. Questions concerning sulphur cycling in the future which will need to be considered in greater detail and which can be partially elucidated by small catchment research, are:

1. acidification of soils, groundwater and surface waters in the tropics;
2. input of sulphur to ecosystems by cloud and fog deposition;
3. internal cycling and leaching from the soil pool of sulphur using ^{35}S or the ratio of stable isotopes $^{34}S/^{32}S$;
4. effects on the sulphur cycle by changes in land-use such as afforestation;
5. effects on soil acidification, loss of nutrients and malnutrition of trees.

The expertise gained in studies at mid-northern latitudes can be applied in designing similar studies in other parts of the world, and in development of integrated monitoring systems.

The rapid industrialization of the tropics is largely increasing the emissions to the atmosphere. Application of pollution abatement devices is scarce in most countries.

The effects of anthropogenic sulphur emissions to tropical ecosystems are virtually unknown. Yet, the combination of increased strong acid loadings with the presence of sensitive soils may lead to fundamental changes in tropical ecosystems (Rodhe *et al.,* 1988).

The effects of sulphur on ecosystems in temperate regions have been well documented by catchment research. It is therefore recommended that a similar approach be initiated in tropical countries. Also the determination of inputs to ecosystems by dry deposition has been facilitated by small catchment investigations. As is the case with dry deposition, cloud and fog deposition are extremely difficult to quantify. The role of clouds in atmospheric inputs to ecosystems can perhaps be elucidated by a combination of foliar and throughfall studies, and monitoring of runoff.

The usage of sulphur stable isotope ratio measurements ($^{34}S/^{32}S$) or ^{35}S labelling in small catchments can be a powerful tool for determining how sulphur is cycled in the soils and taken up by vegetation. So far limited use of ^{35}S in catchments can be expanded to answer questions of SO_2 dry deposition, cycling of sulphur in the soil pool, effects on leaching of soil nutrients related to the speciation and mobility of sulphur in the soil water, root uptake and also for elucidation of foliage losses. All these processes are of fundamental importance for understanding acidification of ecosystems and functioning of the ecosystems. We therefore advocate the greater use of tracers for studying sulphur cycling.

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