MEASUREMENT OF ATMOSPHERIC DEPOSITION UNDER FOREST CANOPIES: SOME RECOMMENDATIONS FOR EQUIPMENT AND SAMPLING DESIGN

ANNE THIMONIER
Swiss Federal Institute for Forest, Snow and Landscape Research, CH-8903 Birmensdorf, Switzerland

(Received 18 March, 1996; accepted 25 February, 1997)

Abstract. Quantification of the forest water flux provides valuable information for the understanding of forest ecosystem functioning. As such, throughfall (and stemflow to a lesser extent) has been frequently measured. Although throughfall collection may seem relatively simple, the requirements to obtain reliable estimates are often underestimated. This review addresses the criteria to take into account when working out the sampling procedure, from the selection of equipment to implementation in the field. Sound sampling of the forest water flux is difficult due to its high spatial and temporal variation. The high costs entailed by the ideal sampling design often prohibit its implementation. Different procedures are available, some of which are compromises between the aim of the study (monitoring or experimental study, short or long term objectives, absolute or relative estimates, quality of the assessment to be achieved) and the available means.

Key words: atmospheric deposition, methodology, sampling, spatial variation, temporal variation, throughfall, stemflow, water chemistry

1. Introduction

Precipitation under forest canopies is frequently measured in forest ecosystem studies. Terms and definitions used to describe it differ, but Parker's (1983) designations have been most commonly used. Two components of the forest water flux are distinguished. Throughfall consists of the water dripping from the canopy as well as the portion of precipitation reaching the forest floor without having being intercepted by the crowns. Stemflow is the water running down the branches and the trunk and depositing at the base of the tree (Parker, 1983). Throughfall usually makes up the major portion of precipitation under the canopy and, as such, is the most commonly measured component of the forest water flux. Stemflow can represent a substantial fraction of the total water input in stands of smooth-barked species with upright branches, but it makes a negligible contribution to the water flux in forests of rough-barked species (Parker, 1983; Brechtel, 1989).

Throughfall and stemflow are two major pathways in forest nutrient cycling, and their quantification is necessary to establish both water and nutrient budgets. Although they may supply less material than litterfall, they constitute a source of dissolved minerals readily available for plant uptake (Parker, 1983). Water and nutrient inputs via throughfall and stemflow influence all soil chemical and biological processes, including pedogenic transformations, turnover of nutrient

Environmental Monitoring and Assessment **52:** 353–387, 1998.

pools, accumulation and mobilisation of possibly toxic substances, and buffering reactions (Mayer, 1987).

Throughfall and stemflow sampling is also useful in assessing and monitoring the pollution climate to which forest ecosystems are exposed (e.g. Johnson and Lindberg, 1992; Matzner and Meiwes, 1994; Meesenburg *et al.*, 1995). Throughfall and stemflow composition does not readily differentiate between the origin of the elements reaching the forest floor, but parallel sampling of the incident precipitation in the open field or above the forest canopy helps discriminate the influence of vegetation (filtering effect of dry and occult deposition and exchange processes) from wet deposition. Derivation of dry deposition from throughfall measurements has been attempted, although not always successfully (Ulrich, 1983; Lovett and Lindberg, 1984; Bredemeier, 1988; Puckett, 1990; Potter *et al.*, 1991; Beier *et al.*, 1992; Joslin and Wolfe, 1992; Draaijers and Erisman, 1993; Brown and Lund, 1994; Neary and Gizyn, 1994; Rustad *et al.*, 1994; Cappellato and Peters, 1995; Reynolds, 1996). However, as the throughfall method has the advantage of being relatively inexpensive and simple compared to other methods directed towards the measurement of more specific pathways of atmospheric deposition (Erisman *et al.*, 1994), it has been used extensively in studies dealing with deposition measurements. Throughfall can provide a valuable quantification of the total inputs to the forest floor of critical chemicals involved in acidification or eutrophication processes, such as nitrogen and sulphur compounds.

It is thus crucial to obtain a representative measurement of throughfall and stemflow, or at least to be aware of the limitations of the estimates. This review focuses on the criteria that should be considered when selecting the type of collector, its design, and the siting in the field. It is more specifically directed towards the requirements in monitoring studies and reviews some of the manuals which have been written to harmonise the sampling procedures at national and international levels. This contribution concentrates on the sampling of precipitation in the wet form; problems related to snow collection are not addressed.

2. Sampling Equipment

2.1. TYPE OF COLLECTOR

2.1.1. *Incident Precipitation and Throughfall*

Wet-only collectors against continuously open collectors. Deposition of atmospheric compounds by rain (wet deposition) is theoretically best measured with specially designed collectors, which are closed by a lid during dry periods and open whenever raindrops (or snowflakes) are detected by a sensor. Such a system prevents the deposition of particles and gases on the walls of the collector during dry periods, as occurs in continuously open collectors. Downwash of the dry-deposited compounds can significantly affect the composition of the sample collected in continuously exposed collector (bulk precipitation) (Erisman *et al.*, 1994; Draaijers *et*

Table I

Examples of bulk/wet concentration ratios taken from the literature (only case studies where the collection interval was the same for both wet and bulk collectors are presented). The given volume corresponds to the cumulative precipitation height in mm over the sampling period. Volume weighted mean concentrations are given in μeq l^{-1}

	Pallanza (Italy)		Den Helder (The Netherlands)		Eskdalemuir (United Kingdom)		Stoke Ferry United Kingdom)		Ithaca (United States)	
	Mosello *et al.*, 1988		Slanina *et al.*, 1979		Stedman *et al.*, 1990		Stedman *et al.*, 1990		Galloway and Likens, 1976	
	Event-based collection		Three day-collection interval		Daily collection		Daily collection		Variable collection intervals (from 7 days to 24 days)	
	wet-only collector	mean bulk/ wet ratio	wet-only collector	mean bulk/ wet ratio	wet-only collector	mean bulk/ wet ratio	wet-only collector	mean bulk/ wet ratio	wet-only collector	mean bulk/ wet ratio
	rain :	1.07								
volume	rain+snow :	1.13	148.9	0.98	1142	1.15	387	1.22	–	1.07
Ca	25	1.31	4.5	1.06	1.7	1.29	3.6	1.55	–	2.00
Mg	7	1.38	8.7	0.87	4.1	1.05	2.5	1.33	–	1.50
K	2	1.00	3.8	1.22	2.3	1.11	2.8	1.09	–	1.10
Na	10	1.03	97.6	1.18	63.0	1.08	34.8	1.36	–	1.20
Cl	12	1.11	125.2	1.14	79.0	1.07	47.4	1.29	–	1.40
NH_4	52	1.06	57.8	1.13	22.1	0.87	67.1	0.80	–	1.10
NO_3	43	1.12	52.0	1.03	19.3	0.93	35.7	1.06	–	1.10
SO_4	80	1.08	26.5	1.02	10.3	0.98	17.2	1.05	–	1.00
H	46	0.98	64.9	0.95	27.0	0.89	25.0	1.16	–	0.92

al., 1996; Table I). Differences in chemical composition of precipitation collected by wet-only and bulk collectors have been assessed in a number of comparative studies (Galloway and Likens, 1976; Galloway and Likens, 1978; Slanina *et al.*, 1979; Soederlund and Granat, 1982 in Slanina, 1986; Dasch, 1985; Mosello *et al.*, 1988; Richter and Lindberg, 1988; Stedman *et al.*, 1990; Bredemeier and Lindberg, 1992). The usually higher precipitation volumes collected by bulk collectors (ratio bulk/wet >1 for precipitation amount, Table I) may be related to the higher aerodynamic blockage by the wet-only collector, reducing catch efficiency (Stedman *et al.*, 1990). The sensitivity of the sensor driving the opening of the lid on wet-only collectors may also influence the precipitation amount that is collected, especially at low precipitation rates. Calcium (Ca), magnesium (Mg), and potassium (K) concentrations are often higher in bulk samples than in wet-only samples, because of the deposition of soil-derived particles on the walls of the collectors during rain-free periods. Differences for nitrogen compounds (nitrate NO_3^-, ammonium NH_4^+) and sulphate (SO_4^{2-}) are usually smaller, but local or regional sources of emissions can significantly influence the composition of bulk samples (Stedman *et al.*, 1990). Part of the differences between wet-only and bulk concentrations may also be the result of delayed opening of the lid at the onset of precipitation, when the concentrations of compounds may be highest: below-cloud scavenging of aerosols and gases in the atmosphere (washout) leads to substantially higher concentrations in rain drops in the early stage of an event (e.g. Hansen *et al.*, 1994; Minoura and Iwasaka, 1996; Burch *et al.*, in press). Wet-only collectors may then underestimate wet deposition (Slanina *et al.*, 1979; Claassen and Halm, 1995a).

A number of studies have been carried out to assess the collection efficiency of various wet-only or wet/dry collectors (collectors with an additional bucket collecting deposition during dry periods) (Galloway and Likens, 1976; Slanina *et al.*, 1979; Bogen *et al.*, 1980; De Pena *et al.*, 1980; Schroder *et al.*, 1985; Graham *et al.*, 1988; Graham and Obal, 1989; Hall *et al.*, 1993; Claassen and Halm, 1995a and 1995b). These studies showed that the performances of the collectors could be quite variable according to the robustness of the device, the tightness of the lid, and the sensitivity of the sensor. Most of all, however, wet-only collectors have the drawback of being expensive and of requiring a power supply. An exception may be the low-cost wet-only device developed by Glaubig and Gomez (1994), involving a counter-weighted cover held in place over the collector by a piece of water-soluble paper; but as the system must be re-installed after the end of each rain event, this collector would be only suitable in regions characterised by heavy rainstorms interrupting long dry periods. The following review concentrates on continuously open collectors only.

Funnels against troughs. Funnel-type gauges are generally used in the open field to measure rain amount and chemistry. Although it has been recommended that collectors of the same design as open-field collectors should be employed for throughfall measurements (e.g. Environmental Data Centre, 1993), no general consensus over this has been reached. A review of studies involving throughfall collec-

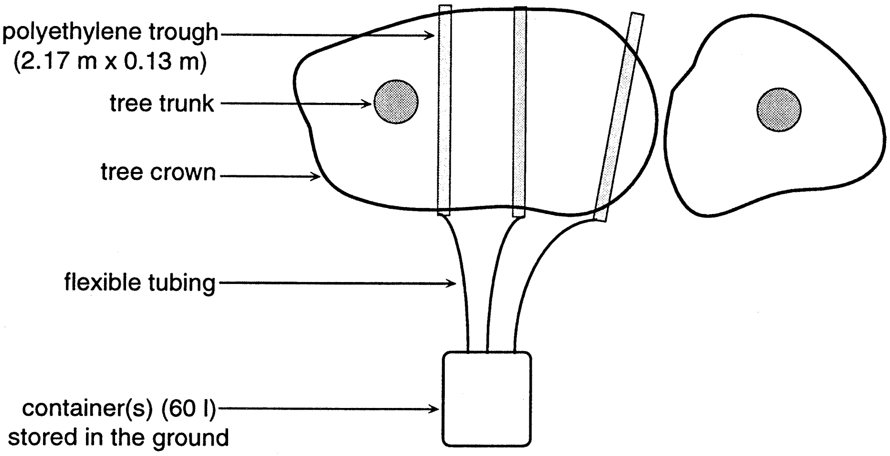

Figure 1. Bird's-eye view of trough-type collectors used in the French network of forest ecosystem monitoring (after Ulrich and Lanier, 1993)

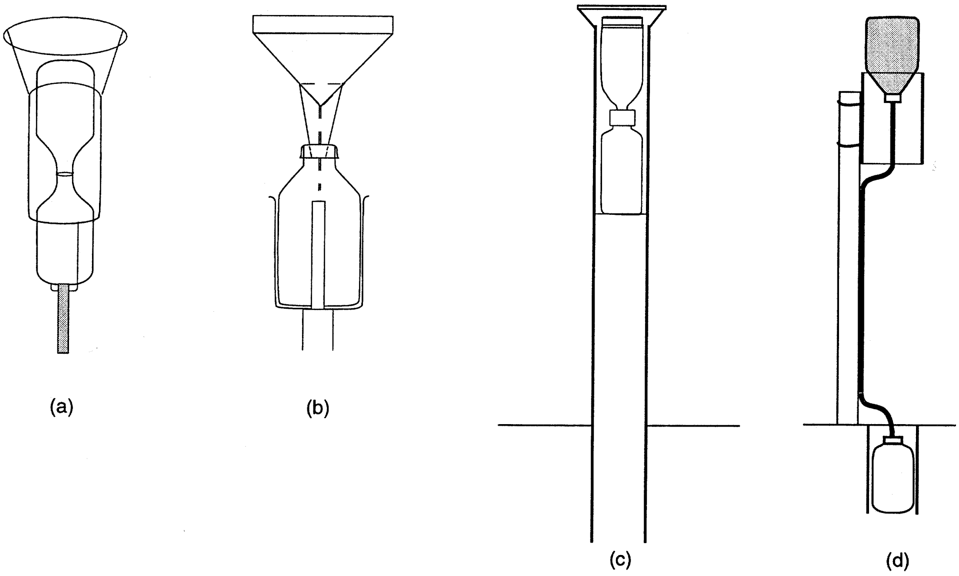

Figure 2. Examples of funnel-type rainwater collectors. (a) Collector proposed by EMEP (1977) and Environmental Data Centre (1993). (b) Collector used in the 'Swedish wet deposition measurement network' (after The Working Group for Environmental Monitoring, 1989). (c) 'Münden 100' collector used in the Hessian Research Programme 'Forest Damage by Air Pollution' (after Brechtel, 1989). (d) Collector used at the Klosterhede research site in Denmark (after Beier and Rasmussen, 1989).

tion reveals that two types of collectors, troughs (Figure 1) and funnels (Figure 2), are in common use. Troughs are believed to collect more representative volumes, as this type of gauge integrates a larger area and thus a variety of canopy conditions (e.g. Reigner, 1964, in Helvey and Patric, 1965; Kostelnik *et al.*, 1989; Draaijers

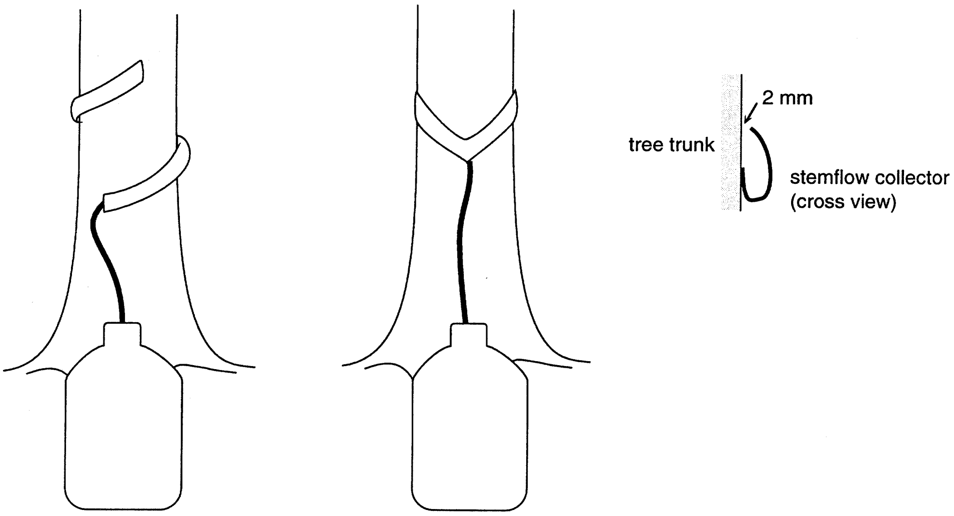

Figure 3. Examples of throughfall collectors: spiral-type and collar-type (after Rasmussen and Beier, 1987).

et al., 1996). The two types of gauge have been compared against each other in a few studies: Reynolds and Leyton (1963, in Crockford and Richardson, 1990) and Hogg *et al.* (1977, ibid.) found that troughs and rain gauges yielded similar mean volumes. Kostelnik *et al.* (1989) obtained significantly larger throughfall amounts in troughs relative to funnels. Crockford and Richardson (1990) also sampled higher volumes with troughs than with standard rain gauges. Conversely, Reynolds and Neal (1991) observed a small bias toward a lower catch in troughs. Troughs were shown to slightly reduce the variance of the estimates (Reynolds and Leyton (1963, in Crockford and Richardson, 1990) and Hogg *et al.* (1977, ibid.), but increasing the collection area by using troughs rather than funnels does not reduce the number of gauges necessary in the same proportions (Helvey and Patric, 1965). Stuart (1962, in Kostelnik *et al.*, 1989) reported that an increase in sampling area of throughfall gauges only slightly reduced the variance of throughfall volume estimates. Potter *et al.* (1991) still needed at least 12 randomly selected 1.0 × 0.1 m trough collectors to stabilise the coefficient of variation for base cation canopy exchange and dry deposition values estimated from throughfall measurements. Generally speaking, although sampling efficiency can vary according to the collector type, the sampling strategy (number and location of collectors) is more important than the type of gauge. Yet, in very heterogeneous canopies inducing a large variability in throughfall distribution, troughs might collect a more representative sample (Weihe, 1976; Crockford and Richardson, 1990).

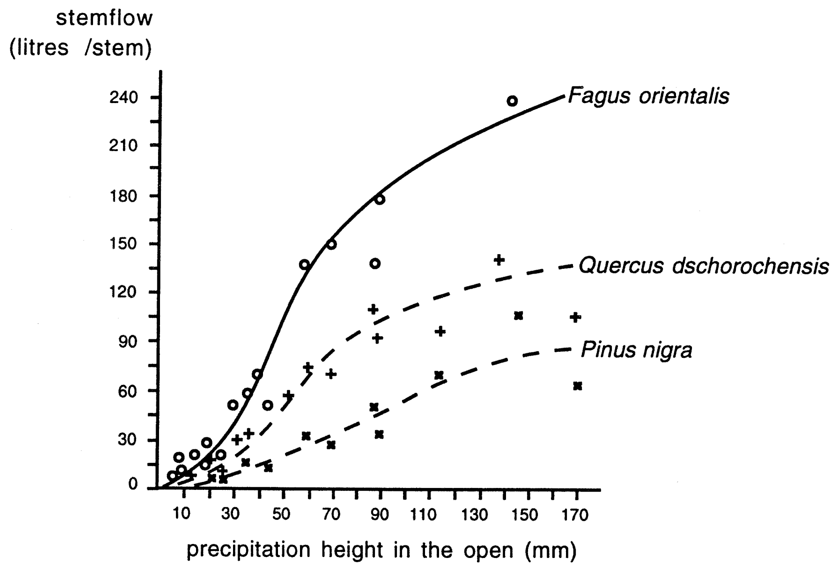

Figure 4. Stemflow amount collected per stem versus height of incident precipitation for three tree species (after Cepel, 1967).

2.1.2. *Stemflow*

Stemflow is traditionally sampled with gutter-like collectors coiled in spiral or collar around the stem of individual trees, and connected to a storage bottle by a tube (Figure 3). As large amounts of stemflow can be collected (Figure 4), the collection vessel must either have a high capacity or consist of several containers of smaller capacity connected in series. An automated tipping-bucket system, allowing continuous recording of volumes and sampling of representative proportional fractions, is probably preferable over the long-term when the sampled species yield large amounts of water.

2.2. DESIGN OF THE COLLECTORS AND SAMPLING ACCURACY

2.2.1. *Incident Precipitation and Throughfall*

Sources of errors. The accuracy required for the measurement of both precipitation amount and chemistry is difficult to achieve using a single type of gauge (Hall *et al.*, 1993). To avoid contamination of the sample by splashing and by wind-raised material from the ground, the collector must be set at a sufficient height, but it then creates an obstacle to the windflow, resulting in a lower catch of the falling precipitation (Rodda *et al.*, 1985; Rodda and Smith, 1986; Sevruk, 1989; Sevruk *et al.*, 1994). The collection is especially biased against snowflakes and fine rain (Rodda *et al.*, 1985). The consequences for precipitation chemistry might be substantial as fine rain drops are more concentrated than drops with greater radii (Bächmann *et al.*, 1993). Wind-field deformation due to a funnel-type gauge can account for 2–10% of water losses for rain and up to 15% for snow according to WMO (1971, in The Working Group for Environmental Monitoring, 1989). Sevruk *et al.* (1994) stated that losses due to aerodynamic blockage could be as large as 3–25% for rain and up to 100% for snow.

Windshields are usually not regarded as a satisfactory solution to the problem in precipitation chemistry sampling, as they can also be a source of contamination. Studies have been dedicated to improve the aerodynamic performance of the collector itself. The value of two parameters describing the change in windflow over the opening of a collector should be reduced (Hall *et al.*, 1993): the relative increase in wind speed measured above the collector inlet (acceleration) and the height of maximum wind speed above the inlet opening relative to the diameter of the inlet opening (called displacement by Hall *et al.*, 1993). Comparing different shapes of collectors with equivalent depth to diameter ratios, Hall *et al.* (1993) showed that funnels induced comparable or greater acceleration, but lower displacement than cylinder-type collectors. Rodda *et al.* (1985) also tested various shapes of gauge and established that a simple funnel yielded rainfall depths which most closely matched those measured by a gauge at ground level.

Beside shape characteristics, the aerodynamic performance of a collector depends on its depth and the ratio of depth to diameter (Hall *et al.*, 1993). Reducing the collector depth reduces the aerodynamic blockage caused by the collector. Shallow collectors however are less efficient in draining the collected sample into the storage vessel, and are much more susceptible to splashing losses. Wind-driven circulation inside the collector may also cause the ejection of collected precipitation, especially in the form of snow or fine rain droplets, as well as increased evaporation from the wetted collector walls. Experiments conducted on cylindrical collectors showed that internal air circulation was highest for a ratio of depth to diameter around unity. With increasing ratios (deeper collectors for a same diameter), ejection of material became increasingly difficult (Hall *et al.*, 1993).

Other sources of errors in the deposition estimates are due to wetting (adhesion of water on the walls of the collector) and evaporation, accounting for 2–10% and 0–4% water losses, respectively, for funnel-type gauges. Wetting and evaporative losses are likely to be higher for troughs due to their larger surface area. The collector should also be designed to prevent rain from splashing in and out. WMO (1971, in EMEP, 1977) recommends that precipitation gauges should comply with the following:

- the area of the aperture should be known to the nearest 0.5% and the construction should be such that this area remains constant;
- the rim of the collector should have a sharp edge and should fall away vertically inside and should be steeply bevelled outside. Sevruk (1989) showed that increasing the thickness of the rim led to an increasing wind speed increment above the opening of a gauge;
- the vertical wall of the collector should be sufficiently deep and the slope steep enough (at least 45°) to prevent loss by splashing and to allow good

drainage. According to Crockford and Richardson (1990), troughs should similarly contain a V-section close to that of the ideal funnel-type gauge;

- the receiver should have a narrow neck and should be sufficiently protected from radiation to prevent loss of water by evaporation.

Diameter of the opening. In the case of funnels, manuals often recommend rather large diameter openings (20–40 cm). When the sampling interval is short, large diameters have the advantage of providing enough solution for analysis (Lewis and Grant, 1978). In forest stands, preference for large diameter funnels additionally results from the reasoning that a larger area will sample a broader variety of canopy conditions (see the above discussion on trough- and funnel-type collectors). However, when the collection frequency is low and when rainfall is potentially high over the defined sampling interval, the large volumes collected by larger openings require high capacity containers, which can be difficult to handle. Some studies have concluded that the sampling area of the collectors had actually a minor influence on the precision of rainfall quantification, as already mentioned in the previous discussion on the type of collector. A few investigations more specifically dealt with the comparison of collectors of the same design but with various collection areas: in forest stands. Weihe (1985) found no significant differences between throughfall amounts collected by 100 cm^2 and 200 cm^2 surface area funnel-type gauges. In the open, Huff (1955) successfully tested several sizes of smaller surface area gauges against standard rain gauges; the results showed that the small orifice gauges could be used in place of the standard gauge without loss of accuracy. These studies were not concerned with the influence of the sampling area on water chemistry; however, these few results support the use of relatively small diameters when the rainfall depth over the sampling period would otherwise require high capacity containers.

The volume of the vessel connected to the funnel or to the trough should be large enough to contain the maximum precipitation amount expected at the sampling location during the defined sampling interval. Commonly, for funnel-type collectors, the diameter of the funnel and the sampling frequency are such that the bottle connected to the funnel has a 2 to 5 l capacity. Figure 2 shows different examples of gauges in use.

Use of a standard rain gauge for more accurate volume estimates. It would be valuable to measure precipitation in the open with both a standard rain gauge and the chosen device so that comparisons can be made of the volumes collected. Such an exercise is useful in the open, where the influence of wind is more critical than in forest stands.

The amount of precipitation recorded by the standard rain gauge enables the correction of the water flux. The use of the values of the standard rain gauge to compute fluxes of elements may however be inappropriate. Concentrations in the collector might be enhanced due to evaporation, and the water amount and concentrations from the same collector should then be used in order to offset this bias. On the other hand, as collection efficiency of non aerodynamically-shaped gauges is biased against more concentrated fine rain droplets, concentrations measured in the collector may be lower than if the collector had the same catch efficiency as a standard rain gauge.

Positioning in the field. In the open field, the opening of the rain gauges must be set horizontal above the ground level rather than parallel to the ground surface. There is no consensus over the height at which the collecting surface should be positioned. The manual of the International Co-operative Programme on Assessment and Monitoring of Air Pollution Effects on Forests (ICP-Forests) (Programme Coordinating Centres, 1994) recommends that the height should be approximately 1.5 m above ground level. The Working Group for Environmental Monitoring (1989) advocates a height of between 1.5 m and 2 m. The manual of the International Co-operative Programme on Integrated Monitoring of Air Pollution Effects (Environmental Data Centre, 1993) recommends 1.20 m. ISO/DIS 4222 (in The Working Group for Environmental Monitoring, 1989) standardised the height at 1.8±0.2 m.

In forest stands, when funnel-type gauges are used, the opening area must be set horizontal, as in the open field. Conversely, troughs must be tilted (25° according to Draaijers *et al.*, 1996) to allow drainage towards the container. This might be an additional factor affecting the water amount sampled (Sevruk, 1989). In the monitoring sites of the Nordic countries, collectors have been set directly on the ground or on a short pole (0.5 m) (The Working Group for Environmental Monitoring, 1989). The ICP-Forests manual (Programme Coordinating Centres, 1994) recommends however that the opening area should be raised to a height of approximately 1 m over the ground level to avoid contamination by soil.

2.2.2. *Stemflow*

High volumes of stemflow are usually collected from each sampled tree (Figure 4). Rasmussen and Beier (1987) suggested that the wide opening of some collecting devices led to an overestimation of the amounts of stemflow by including a fraction of throughfall. It might be advisable to adjust the very small diameter slit (2 mm) they recommend (Figure 3) to the species sampled. The opening should also not be blocked too easily.

The stemflow collectors should be placed around the stem of the trees between 0.5 m and 1.5 m above ground level (Programme Coordinating Centres, 1994). Care should be taken not to damage the bark, as stem exudates may contaminate the sample.

2.3. MATERIAL

Whatever the type of collector chosen, all components should be made of chemically inert material. Quality Teflon (with smooth surfaces) is ideal but is expensive. Alternatively, polyethylene is recommended for analyses of macro-ions in most monitoring manuals, and has been used extensively. Polyethylene retains dry-deposited particles more efficiently than Teflon surfaces (Dasch, 1985), and the composition of bulk precipitation may thus be more influenced by dry deposition when polyethylene collecting surfaces are used; but adsorption of gaseous SO_2, NO_2 and HNO_3 on polyethylene surfaces is insignificant, unless the surface is wet (Dasch, 1985). Collection of precipitation for trace metals analysis is possible in polyethylene gauges but then a special cleaning procedure of all vessels is required, and samples have to be acidified in the collection bottles to re-mobilise the cations adsorbed on the walls. For special studies involving analysis of organic components, Teflon or glass should be used (EMEP, 1977). Glass is not suitable for other elements as the glass surface can act as an ion exchanger. It is also prone to breakage (Galloway and Likens, 1976; 1978).

The collectors should be washed in acid and thoroughly rinsed with deionised water after each sampling (Galloway and Likens, 1978). Washing is especially recommended when the storage vessel has a small capacity, as the error due to contamination by any remaining solution in the container is then proportionally higher.

Silicon rubber has suitable chemical and physical properties for the gutter-like component of the stemflow collectors. Polyethylene foam has also been used (e.g. Ulrich and Lanier, 1993). Silicone sealant can be used to attach the collector to the tree trunk. The flexibility of this material prevents the stem from being damaged in the short term. However, on long-term monitoring sites, in view of tree growth, the collecting device should be occasionally replaced.

3. Conservation in the Field and Collection Frequency

Contamination by coarse material. During the collection period the sample is exposed to contamination by coarse material such as insects or leaves. This contamination risk can be minimised by a net fitted at the junction between the collecting part of the device and the storage bottle or the tube leading to it. Small glass beads (Brechtel, 1989) or glasswool have also been used. Glasswool has the disadvantage of presenting a large surface area which could adsorb dissolved substances (Lewis and Grant, 1978). The nets used as filters may have the drawback of providing an environment favourable to the growth of algae which may influence nitrogen transformations (Ferm, 1993). The mesh size should not be too small (>0.25 mm according to Draaijers *et al.*, 1996), to limit humidity retention and subsequent evaporation. A sufficiently large mesh size also reduces the chance of the filter becoming clogged. With stemflow collectors, a narrow gutter opening has the advantage of reducing the risk of collecting organic debris. Another source of contamination is bird droppings. On funnel-type collectors, guard rings mounted a few centimetres from the collecting surface (Figures 2a and 2c) have been a successful preventative measure.

Biochemical changes over the sampling interval. The concentration of some elements or compounds can vary over time due to biochemical reactions in the sample. Several studies have been concerned with the effects of the length of the collection interval on the sample's chemical composition. In these studies, samples collected from shorter intervals are compared to samples collected after a longer period in the field. In the following, 'event samples' refer to samples collected after every precipitation event, 'daily', 'weekly', 'biweekly' or 'monthly' samples relate to samples collected after 24 h, one week, two weeks, one month, respectively.

Some studies report only a minor influence of the collection interval. Madsen (1982) compared wet-only precipitation volume and element concentrations from daily, weekly and biweekly collection intervals in Florida (U.S.A.); volume-weighted averages from daily samples over one or two weeks were not significantly different from measured values on the corresponding weekly or biweekly samples. In Ithaca (U.S.A.), Galloway and Likens (1976) obtained a good agreement between bulk deposition estimated from summed amounts of samples collected after every rain event and deposition assessed from collectors emptied after 2 to 4 weeks in winter. Under Scandinavian conditions, Granat (1974, in Slanina *et al.*, 1987) reported that precipitation samples were stable for at least one month. In The Netherlands, Slanina *et al.* (1987) found no clear indication of changes which could be ascribed to biological activity in wet-only subsamples of a precipitation event kept in the field for different time intervals (0 to up to 86 days). More commonly, however, significant alterations of the chemical composition of precipitation with lengthening of the collection intervals have been observed. Phosphorus and nitrogen compounds are especially unstable (Draaijers *et al.*, 1996). Van der Maas and Valent (1989) observed increased ammonium concentrations in their throughfall samples which they related to ammonification, but reports of decreasing ammonium concentrations over time are the most frequent (Galloway and Likens, 1978; de Pena *et al.*, 1985; Sisterson *et al.*, 1985; Tang *et al.*, 1987; Liechty and Mroz, 1991; Ferm, 1993). The changes have been ascribed to transformations into organic forms by micro-organisms or to nitrification (Liechty and Mroz, 1991; Ferm, 1993). Ammonia (NH_3) exchanges and adsorption on the walls of the container were also suggested as possible causes for the decrease in ammonium concentration (Müller *et al.*, 1982; de Pena *et al.*, 1985), as storage in the dark and at cold temperatures (>0 °C), conditions under which biological activity is inhibited, yet was insufficient to prevent losses (Müller *et al.*, 1982). Finally, although Ferm (1993) found negligible denitrification as measured by changes in N_2O content of the air above his throughfall samples, denitrification might be an additional factor accounting for nitrogen losses under certain conditions, as suggested by Draaijers *et al.* (1996).

pH also varies with storage time in the field. Liechty and Mroz (1991) observed a decrease in pH in their throughfall samples, which they attributed to the production of protons (H^+) associated with ammonium transformations. The opposite trends for pH have also been observed. Burch *et al.* (in press) measured higher pH on precipitation samples in the laboratory than expected from the weighted mean of pH measured in the field on sequentially sampled events. Camuffo *et al.* (1988) similarly observed an increase in pH some hours after the rain event. Sisterson *et al.* (1985) and de Pena *et al.* (1985) found that pH of weekly wet deposition samples was higher than precipitation-weighted average pH from event samples over the corresponding week. Several possible causes for this pH increase have been suggested: slow dissolution of alkaline (Ca, Mg, K) soil or dust particles (Peden and Skowron, 1978; Sisterson *et al.*, 1985; Camuffo *et al.*, 1988), consumption of organic acids by micro-organisms in the sample prior to analysis in the laboratory (Keene and Galloway, 1984), neutralisation by the polyethylene vessels (Peden, 1988, in Bigelow *et al.*, 1989), and field handling (Bigelow *et al.*, 1989). In some cases, seasonal trends were observed (Keene and Galloway, 1984; Bigelow *et al.*, 1989): higher neutralisation in summer was associated with the disappearance of organic acids initially in larger concentrations (associated with organic matter production during growing season).

Calcium and magnesium concentrations in wet precipitation samples can increase (Sisterson *et al.*, 1985), while de Pena *et al.* (1985) observed lower Ca and Mg concentrations with time. Evolution of Ca and Mg concentrations may be controlled by two processes acting oppositely: slow dissolution of soil particles and biological uptake. Sulphate concentrations may be influenced by exchanges with gaseous SO_2 in the atmosphere above the sample (Sisterson *et al.*, 1985). Lastly, contamination during sample handling and evaporation may also partly account for the increase in the concentrations of some elements. Volume losses with longer sampling intervals have been observed by Galloway and Likens (1978), de Pena *et al.* (1985), Liechty and Mroz (1991).

The diversity of conclusions from these studies may be related to the variety of conditions prevailing at the study sites or during the period of investigation (climate, local sources of contamination, and measures adopted to improve sample conservation in the field). The type of sample examined (bulk precipitation, wet deposition, throughfall) may also influence the results: Peden and Skowron (1978) showed that the chemical composition of precipitation sampled by a wet/dry device was more stable over time than that of samples from continuously open collectors. Lastly, the initial chemical properties of the precipitation sample may partly control its evolution: acidic precipitation is unfavourable to biological activity and may impede changes in the sample (Galloway and Likens, 1976); high nitrogen concentrations in the sample may be a pre-condition for nitrification of ammonium to take place (Liechty and Mroz, 1991).

Preventative measures against changes in chemical composition in the field. In view of sample instability, event-based or weekly collection of the samples is best. This improves the estimation of nutrient fluxes, as data variance increases with longer collection intervals (Kimmins, 1973; Galloway and Likens, 1978), due to increased probability for contamination, evaporation, and chemical or biological changes. Furthermore, samples with higher concentrations due to contamination are best detected over a shorter collection interval (Slanina *et al.*, 1990). Sampling over a longer period leads to a 'dilution' of the error caused by a single event, and thus to a general overestimation of deposition. Lastly, the consequences of possible data loss (due for instance to contamination) on the quality of the monitored time series are smaller when sampling intervals are shorter (Programme Coordinating Centres, 1994).

Very often, however, the sampling frequency must be lowered for logistic reasons. Biological activity in the water sample can then be reduced by shielding the collectors from sunlight and preventing warming. Storage of the collectors in the ground meets these requirements, but the collecting surfaces must be raised to avoid contamination by splashing. Tubes can be used for this purpose (Figures 1 and 2d). However, the use of tubes is inadvisable when careful cleaning is necessary. Cleanliness of all parts of the collecting device is especially critical in the case of funnel-type gauges, which sample lower volumes of water than troughs. As an alternative to storage in the ground, funnel-type collectors can also be wrapped in aluminium foil, or painted black (Ferm, 1993). Storage inside PVC pipes has also been suggested (Brechtel, 1989; Figure 2c). Non-volatile chemical preservatives can be added, but they should not interfere with the elements being measured or they should be added in known amounts which can later be taken into account. Galloway and Likens (1978) tested a variety of preservatives ($CuSO_4$, Na_2SO_3, $Na_2S_2O_5$, HCHO [formaldehyde], CH_3OH [methanol], $CHCl_3$ [chloroform], $C_6H_5CH_3$ [toluene], $Hg(Ac)_2$ [mercuric acetate]). All these biocides had disadvantages, because of contamination (with the active compound or with impurities in the reagent), reactions with the solutes in the sample, or interference with the analytical method. Iodine has been further suggested as preservative as it has a low vapour pressure and is not harmful to the environment. Ferm (1993) added 0.5 g of iodine to 5 l collection bottles before each sampling interval. Comparison of collectors with preservatives against black collectors without preservatives showed however that keeping collectors dark impeded nitrogen transformation quite effectively (Ferm, 1993). The use of preservatives can therefore be seen as an additional precaution. In any case, electrical conductivity and pH will be modified by the addition of preservatives. However, to evaluate the degree of transformation of particular molecules, such as nitrogen compounds, it may be of interest to run two parallel collectors, one with preservative and one without. Measurement of organic nitrogen in addition to the analysis of the mineral forms may also provide useful information about total input for this element.

Whatever the sampling frequency chosen, it should be the same for all measurements (throughfall, stemflow and open field precipitation).

Storage in the laboratory prior to analysis. pH and conductivity should be measured immediately after arrival of the samples if not performed in the field. Samples should then be filtered at 0.45 μ as soon as possible. Filtering significantly improves sample conservation, partly by removing soil-derived particles, which otherwise slowly dissolve in the sample or act as a cation exchange medium (Peden and Skowron, 1978). Storage at 4 °C in the dark is then usually considered sufficient, although Müller *et al.* (1982) stated that only freezing could impede ammonium losses during storage.

4. Sampling Design

4.1. THROUGHFALL

4.1.1. *Spatial Variation of Throughfall*

Throughfall amount and quality can vary according to site conditions (Parker, 1983; Reynolds *et al.*, 1989; Nordén, 1991), tree species, stand structure, stand age, tree vitality, or phenological stage (e.g. Parker, 1983; Levett *et al.*, 1985; Carleton and Kavanagh, 1990; Potter *et al.*, 1991; Draaijers *et al.*, 1992; Van Ek and Draaijers, 1994). Proximity of aerosol, dust or gas sources (Parker, 1983) and direction of prevailing winds can influence deposition fluxes (Beier *et al.*, 1993). Distance from the forest edge is also a strong factor of variation, with effects being apparent over a range of up to 100 m (Hasselrot and Grennfelt, 1987; Draaijers *et al.*, 1988; Beier and Gundersen, 1989; Ferm, 1993; Neal *et al.*, 1994; Thimonier, 1994). Volume and chemistry are thus highly variable in space, from local to regional scales.

Variation at the tree scale. At the tree scale, measurements at various distances from the stem display strong intra-tree variations for fluxes and concentrations (Stout and McMahon, 1961; Aussenac, 1970; Ford and Deans, 1978; Freiesleben *et al.*, 1986; Edwards *et al.*, 1989; Carleton and Kavanagh, 1990; Johnson, 1990; Pedersen, 1992; Beier *et al.*, 1993; Hansen, 1995; Seiler and Matzner, 1995). In some stands with tree species having a well-defined and systematic branch structure, such as Norway spruce (*Picea abies* (L.) Karst.) or Sitka spruce (*Picea sitchensis* (Bong.) Carr.), this spatial variation across the crown shows consistent patterns which can be modelled as a function of the distance from the trunk (Aussenac, 1970; Ford and Deans, 1978; Johnson, 1990; Pedersen, 1992; Beier *et al.*, 1993; Hansen, 1995). Ford and Deans (1978) measured greater amounts of throughfall close to the tree stems in a 14-year-old *Picea sitchensis* plantation. Conversely, Johnson (1990) obtained higher throughfall volumes at the crown edge of 50-year-old *Picea sitchensis* trees. Pedersen (1992) also found increasing throughfall amounts as well as decreasing concentrations from the stem to the canopy edge in a 30-year-old *Picea sitchensis* stand. A similar increase in throughfall amount with increasing distance from the stem was obtained in *Picea abies* stands (Aussenac, 1970; Beier *et al.*, 1993; Hansen, 1995) and Scots pine (*Pinus sylvestris* L.) and grand fir (*Abies grandis* (Dougl.) Lindl.) stands (Aussenac, 1970). These gradients seem to be steeper in young conifer stands, with homogeneous circular crowns, than in mature stands characterised by heterogeneous crown structure (Seiler and Matzner, 1995). Devices have been designed to integrate this non-random intra-tree variability, with collecting surface areas proportional to the projected area of the crown at increasing distance from the stem (Rasmussen and Beier, 1987; Beier and Rasmussen, 1989; Figure 5). However, the use of this type of device is limited

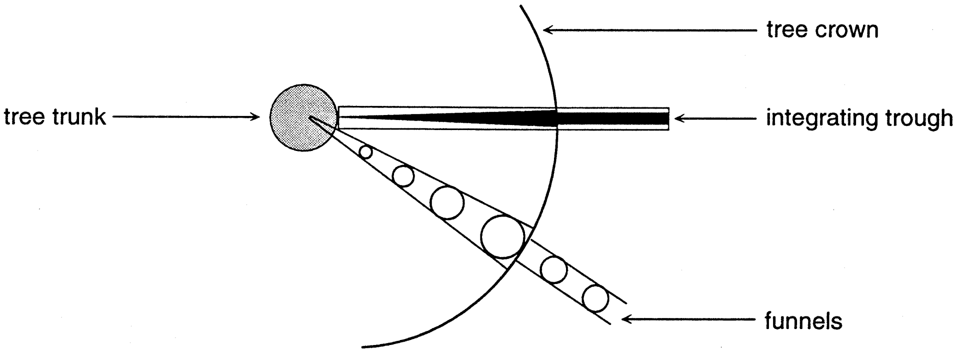

Figure 5. Non-random throughfall collection by integrating trough or funnels with varying diameters (after Rasmussen and Beier, 1987).

because its design must be adapted to the sampled tree, and because wind may cause drift of incoming water from areas other than directly above the collector. Furthermore, a single device of this type is insufficient to sample the variability of the stand, which has been shown to be substantial at the small plot scale (Robson *et al.*, 1994). Variability is also important in uniform even-aged stands: in a 40-year-old *Picea abies* plantation, Beier *et al.* (1993) observed a strong tree-to-tree variability which was related to tree height and diameter.

Variation at the stand scale. The number of gauges necessary to cover the spatial variability at the stand scale and provide reliable estimates of throughfall deposition has been estimated in a few studies. These studies involve a number of collectors considered sufficiently large to allow the assumption that they provide the 'true' mean of the investigated throughfall parameter. Several approaches have then been used.

A first method consists of calculating the range of variation of the estimates for the investigated parameter for increasing numbers of collectors. Estimates are computed from repeated combinations of randomly selected collectors ranging from 1 to the total number of collectors. Results are plotted to visualise the rate of improvement of the estimates with increasing numbers of collectors. This method has been applied by Czarnowski and Olszewski (1970), Kimmins (1973), Puckett (1991), Lawrence and Fernandez (1993). Czarnowski and Olszewski (1970) found that for an old-growth oak stand, 30 gauges could be used to obtain a reliable estimate of throughfall volume. Similarly, in a 30 to 40-year-old western hemlock – western red cedar (*Tsuga heterophylla* (Raf.) Sarg. – *Thuja plicata* Donn) stand, Kimmins (1973) found that the rate of improvement of the estimate of the mean throughfall amount slowed down significantly beyond 30 collectors. In a deciduous stand (*Quercus* sp.), Puckett (1991) showed that the rate of improvement of the estimates was high during the addition of the first 10 collectors, then considerably slowed down beyond 20 collectors. Lawrence and Fernandez (1993) computed the minimum and maximum estimates of the mean deposition for the sampling month with median variation. The number of collectors required to achieve convergence of the estimates with a given precision (in percentage of the mean) was then determined. In a spruce-fir forest, nutrient deposition on a seasonal or annual basis could be estimated with 20 to 30 collectors within 20% of the mean. Examination of the evolution of the variation coefficient (instead of the mean) with increasing numbers of collectors has also been used to determine the number of collectors required. Duijsings *et al.* (1986) thus found that in order to obtain annual deposition estimates within 10% of the mean (calculated from 11 collectors only), at least 5 collectors were required for calcium and sulphate, 8 for hydrogen.

A second method was developed by Peterson and Rolfe (1979). They analysed the throughfall volumes collected in a deciduous forest by 96 fixed collectors for 12 precipitation events distributed over a whole year. Mean throughfall volume and standard deviation were determined for several combinations of different numbers of collectors. From this set of data, for each season, a regression of the standard error in percent of the mean against the necessary number of samples was established. With this method 14 collectors were necessary to achieve a standard error of 5% of the mean in summer, 5 collectors in winter. Higher variability in summer was ascribed to the foliage, which provided more sheltered areas or drip points in the canopy than the branches alone.

A third method, most widely applied (Kimmins, 1973; Weihe, 1985; Kostelnik *et al.*, 1989; Puckett, 1991; Lawrence and Fernandez, 1993; Seiler and Matzner, 1995), consists of calculating the number of collectors necessary for a given confidence interval and precision, using the following equation

$$n = \frac{t^2_{\alpha,\mathrm{n}-1}\, C^2}{\mathrm{E}^2} \tag{1}$$

where

n = number of collectors;
$t_{\alpha,n-1}$ = Student's *t* value at the α level;
C = coefficient of variation;
E = acceptable error (desired confidence interval), as a percentage of the mean.

Helvey and Patric (1965) applied a particular case of Equation (1), with a 68% confidence interval (t=1), by calculating the sample size with Equation (2)

$$n = \text{(standard deviation/standard error)}^2 \tag{2}$$

As pointed out by Kimmins (1973), Equation (2) is based on a desired standard error, not on a desired confidence interval. Equation (2) yields a lower number of necessary collectors than Equation (1).

From Equation (1), under comparable mixed-hardwood forest canopies, Kostelnik *et al.* (1989) and Puckett (1991) obtained a number of respectively 14 and 11

Table II

Average number of throughfall collectors needed to estimate ion concentrations and precipitation volume at the 95% confidence level within 10% of the mean. 1. Under mixed-hardwood canopies (Kostelnik *et al.*, 1989 and Puckett, 1991), 2. under a spruce-fir canopy (Lawrence and Fernandez, 1993) and 3. under a *Picea abies* canopy (Seiler and Matzner, 1995)

	Kostelnik *et al.*, 1989 (6 precipitation events) mean (standard deviation)	Puckett, 1991 (5 precipitation events) mean (standard deviation)	Lawrence and Fernandez, 1993 (using median coefficient of variation for 23 monthly samples)	Seiler and Matzner, 1995 (samples mixed over a 6 month period)
Volume	14 (5)	11 (3)	24	1
H^+	48 (27)	41 (39)	68	47
Ca^{2+}	179 (78)	64 (82)	168	41
Mg^{2+}	177 (65)	72 (56)	208	45
K^+	382 (226)	106 (58)	122	35
Na^+	132 (101)	71 (54)	105	72
Cl^-	152 (78)	104 (100)	90	143
Mn^{2+}	–	65 (46)	–	44
SO_4^{2-}	69 (74)	20 (18)	43	54
NH_4^+	69 (57)	310 (502)	208	23
NO_3^-	13 (6)	19 (14)	221	31
DON[a]	–	–	–	23
Total N	–	–	–	17
DOC[b]	–	–	141	–

[a] DON: dissolved organic nitrogen.

[b] DOC: dissolved organic carbon.

collectors on average to estimate the mean volume within 10% at the 95% confidence level (Table II). In a mature *Picea abies* stand, Seiler and Matzner (1995) calculated that one collector would be sufficient to estimate the average throughfall amount with the same precision and confidence level; however, in their calculations, they used samples pooled in proportion to the volumes over the 6-month sampling period; conversion into seasonal or annual values decreases the spatial variation of throughfall deposition, as the influence of values for shorter time intervals with atypically high variability is decreased when these values are summed (Duijsings *et al.*, 1986; Lawrence and Fernandez, 1993). Other factors may affect the results. For example, the number of gauges necessary to estimate throughfall amount is higher in the case of low intensity and short duration precipitation events, when water saturation of foliage is not reached (Helvey and Patric, 1965; Aussenac, 1970). Asymptotic decreases in variation coefficients for throughfall amount estimates with increasing incident precipitation have been observed by several authors (Aussenac, 1970; Kimmins, 1973; Duijsings *et al.*, 1986; Loustau *et al.*, 1992). Yet no clear pattern of variation of the coefficient of variation for the concentrations of elements with throughfall volumes was observed (Kimmins, 1973; Duijsings *et al.*, 1986); the number of gauges required to estimate element concentrations will thus vary independently of the throughfall volume. This minimum number for estimates of nutrient concentrations or fluxes is usually much higher than for estimates of throughfall amount (Kimmins, 1973; Levett *et al.*, 1985; Duijsings *et al.*, 1986; Kostelnik *et al.*, 1989; Puckett, 1991; Lawrence and Fernandez, 1993; Seiler and Matzner, 1995; Figure 6 and Table II). It is especially high on sites with a heterogeneous structure of the canopy: in a young *Pinus radiata* D. Don plantation and a *Nothofagus truncata* stand, Levett *et al.* (1985) calculated that a precision of 10% of the mean annual flux for the most variable element could be achieved with 30 throughfall funnel-type collectors on an annual basis, whereas substantially greater numbers of collectors were necessary in the case of a thinned *Pinus radiata* plantation or a very heterogeneous Podocarp-hardwood forest. Seasonally induced patchy structure may also significantly increase the required sample size (Duijsings *et al.*, 1986).

The large sampling effort required in terms of number of collectors has led to the development of alternate methods. The ‘roving’ collectors system was first proposed by Wilm (1943, in Kimmins, 1973) to reduce the number of collectors on the plot. In this method, collectors are randomly relocated after each collection interval and data are adjusted by regression on the incident precipitation over the collection interval, so that the mean can be calculated for the entire period of study with the whole set of data. The validity of this method relies on the strong correlation between incident precipitation and throughfall volumes. Kimmins (1973) tested the application of Wilm’s (1943) method to the study of chemical concentrations and fluxes under the canopy, but the poorer correlations between throughfall and incident precipitation obtained when chemical parameters were considered rendered this method inapplicable under the conditions of the study. Derivatives of

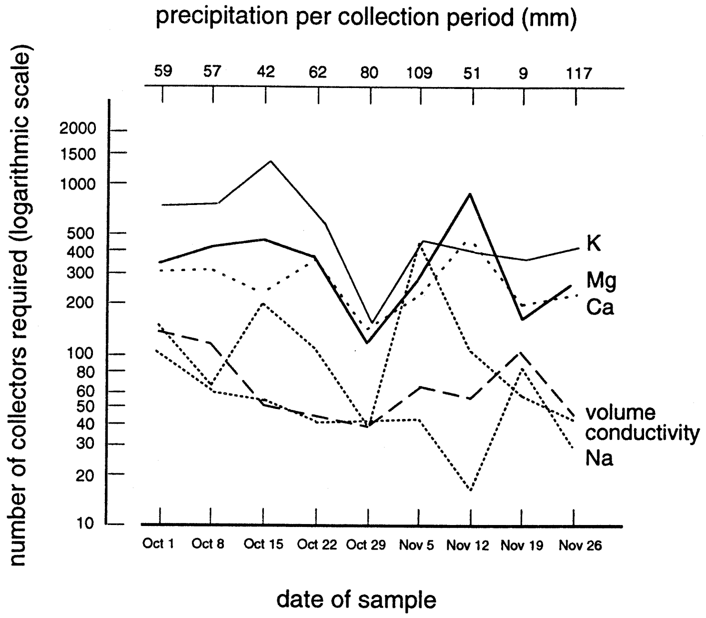

Figure 6. Number of throughfall collectors needed to estimate concentrations, volume and conductivity with a 95% confidence interval equal to 5% of the respective means in a 30–40-year-old Tsuga heterophylla – Thuja plicata stand (after Kimmins, 1973).

Wilm's (1943) method have been developed. In a two-year study, Attiwil (1966, in Kimmins, 1973) used three collectors, one being fixed while the other two were randomly relocated every second week after sample collection. Regression analyses of the values obtained from the roving collectors against the values from the fixed collector were used to estimate concentration values for each period. This method assumes a stable relationship between values from the fixed collector and the 'true' mean. Kimmins (1973) found however that the ranking of the collectors based on concentration or deposition values was very unstable from a collection interval to another. He also tested the relationship between values from a variable number of roving collectors (2 to 10) against values from one fixed collector. A large scatter in the data compromised the validity of the regression (in terms of accuracy) when few collectors or a short period of investigation restricted the numbers of available samples. Lloyd and Marques (1988) showed that the error term due to sampling a fraction of the area with *n* fixed gauges could be reduced by relocating the collectors *m* times. Mathematically constructed curves relating errors in mean throughfall amount estimates to the number of random arrangements for various numbers of gauges gave theoretical values consistent with real data. The roving method may be unsuitable when the objective is the study of short-term variation of throughfall, but estimates at the plot-scale for a longer period are substantially improved. In any case, relocation of the collectors reduces biases due to sampling of a restricted fraction of the canopy (Neal *et al.*, 1994).

Manuals for monitoring programmes give a guideline number of 4–10 collectors per 0.1 ha as a sampling density that is commonly applied (The Working Group for Environmental Monitoring, 1989; Environmental Data Centre, 1993). The ICP-Forests manual (Programme Coordinating Centres, 1994) advocates a pre-study of the variation within the plot to determine the required number specifically for the studied site, using one chemical parameter. However, the number that is necessary varies strongly according to the parameter being studied. It also fluctuates considerably with the sampling interval or the precipitation event for which it is computed (Kimmins, 1973; Kostelnik *et al.*, 1989; Puckett, 1991; Figure 6 and Table II).

Spacing of the collectors. Czarnowski and Olszewski (1970) found that the mean throughfall amount did not depend on the spacing of the gauges when these were placed at regular intervals (1 m) along a 100 m transect in a old-growth oak forest. Using 52 fixed throughfall gauges distributed over a 50 m × 50 m area in a maritime pine (*Pinus pinaster* Ait.) plantation, Loustau *et al.* (1992) detected no spatial autocorrelation between measurements of throughfall amounts. The random distribution of drip zones in the canopy can induce large differences in throughfall amount collected by two collectors only 1.5 m apart (Puckett, 1991). Brechtel (1989) recommended that the distance between adjacent gauges should be two thirds of the average spacing of the trees. When the number of collectors used is limited, however, it may be preferable not to place the collectors too close to each other, in order to limit the risk that the sampled canopy might change dramatically due to changes affecting one single tree. In any case, the structure of the canopy sampled by the collectors should be documented.

4.1.2. *Siting on Plots Designed for Long-Term Ecosystem Research*

In ecosystem studies or in long-term studies involving a number of plots, the whole area of large plots (>1 ha) cannot be sampled. This is because disturbance to other ecological measurements needs to be avoided, and because the large number of collectors would be unmanageable. The location of the collectors must therefore be restricted to a smaller area, even though extrapolation to the whole stand could result in errors. In a homogeneous *Pinus sylvestris* plantation, such errors have been found to be as high as 20% for water input (Cape, 1989).

The position of this sub-plot can be determined on the basis of the other ecological measurements carried out on the site. A random component can also be included in the selection, as well as subjective considerations (presence of a visible environmental gradient such as a slope). On the delimited subplot, random or systematic siting of the collectors, or a combination of both, is recommended. Systematic sampling is satisfactory as long as the studied stand does not display any systematic pattern (such as plantation rows). Some examples of placement of the collectors are given Figure 7. Stratification by canopy structure or tree size has

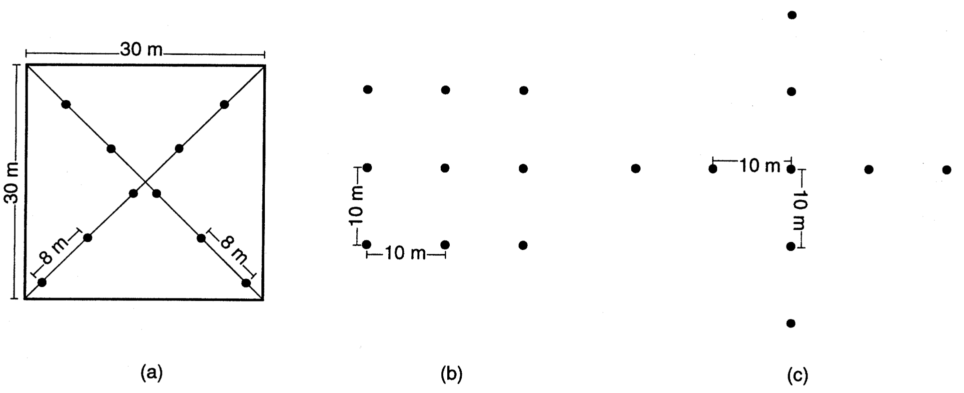

Figure 7. Examples of systematic siting of the throughfall collectors in a plot (after Programme Coordinating Centres, 1994 (a) and Environmental Data Centre, 1993 (b and c)).

also been suggested (e.g. Aussenac, 1968; Levett *et al.*, 1985), but should not be used at too fine a scale. Although systematic patterns of interception related to the stand structure can be observed (Robson *et al.*, 1994), fixed collectors can sample highly variable throughfall amounts or chemistry from one precipitation period to another, as determined by variations in wind speed and direction or rainfall intensity (Kimmins, 1973; Weihe, 1985; Robson *et al.*, 1994).

A subjective sampling design has been favoured in some studies where the number of collectors that could be managed was low. Collectors were installed under a tree or a group of trees typical of the stand (average age, diameter, height) in such a way that the sampled area was representative of the respective gap and canopy proportion (e.g. Atteia and Dambrine, 1993), or even took into account the spatial gradient of concentrations along the crown projection (Ulrich and Lanier, 1993; Figure 1). Such a sampling design enables relatively easy maintenance, and restricts trampling in the plot, an important point when the site is visited on a frequent basis and monitored over the long-term. However, in view of the substantial spatial and temporal variation of throughfall chemistry, this type of design should not be applied when logistics enable a greater number of collectors.

4.2. STEMFLOW

4.2.1. *Pre-Assessment of the Needs for Stemflow Measurement*

Stemflow collection represents significant additional costs in the estimation of the forest water flux. It is complicated by the large volumes involved, and sampling devices are not always entirely satisfactory (due to the risk of leakage or blockage). Stemflow gauges badly attached to the stem could also damage the tree. Because of all these problems, the sampling effort may not be justified in stands where stemflow makes only a minor contribution to the flux.

Table III

Some examples of throughfall and stemflow amounts as a percentage of incident rainfall

Stand composition	Age (yr)	Stem density (stems/ha)	Sampled trees	Incident rainfall (mm)^{b}	Throughfall	Stemflow	Reference
Fagus sylvatica L., *Carpinus betulus* L.	30	1300	14	724	76%	7%	Aussenac (1968)
Fagus sylvatica L.	50	599	2	1528	66%	9%	Ulrich *et al.* (1995)
Fagus sylvatica L.	90	374	2	943	79%	8%	Ulrich *et al.* (1995)
Fagus sylvatica L.	80–100	576	2	2618	90%	27%^{d}	Ulrich *et al.* (1995)
Fagus sylvatica L.	100	240	2	1013	71%	11%	Nihlgård (1970)
Fagus orientalis Lipsky	46	–	5	1045	67%	16%	Cepel (1967)
Fagus grandifolia Ehrh.	[all ages]	–	7	340	66%	10%	Voigt (1960)
Quercus petraea (Mattus.) Liebl.	29	5000	6	1637	74%	10%	Cape *et al.* (1991)
Quercus petraea (Mattus.) Liebl.	40–120	158	7	1717	88%	2%	Carlisle *et al.* (1966, 1967)
Quercus petraea (Mattus.) Liebl.	120	182	2	1222^{c}	71%	<1%	Nizinski and Saugier (1988)
Quercus dschorochensis Koch	50	–	3	1020	69%	11%	Cepel (1967)
Quercus prinus L. (main species)	–	–	^{a}	1260	88%	5%	Johnson *et al.* (1985)
Hardwood (main species: *Acer saccharum* Marsh.)	–	–	16–25	1023	82%	3%	Neary and Gizyn (1994)
Alnus glutinosa (L.) Gaertn.	29	2510	6	1637	74%	9%	Cape *et al.* (1991)
Liriodendron tulipifera L. (main species)	–	–	^{a}	1260	97%	3%	Johnson *et al.* (1985)
Picea abies (L.) Karst.	29	3200	6	1637	71%	14%	Cape *et al.* (1991)
Picea abies (L.) Karst.	30	2160	6	816	64%	2%	Aussenac (1968)
Picea abies (L.) Karst.	55	880	2	1013	58%	3%	Nihlgård (1970)

Table III
Continued

Stand composition	Age (yr)	Stem density (stems/ha)	Sampled trees	Incident rainfall (mm)^b	Throughfall	Stemflow	Reference
Picea sitchensis (Bong.) Carr.	14	3590	10	1639	43%	27%	Ford and Deans (1978)
Picea sitchensis (Bong.) Carr.	24	3600	6	1005	67%	14%	Cape *et al.* (1991)
Picea sitchensis (Bong.) Carr.	50	970	9	2130	69%	3%	Johnson (1990)
Pinus sylvestris L.	26	2700	6	1005	76%	9%	Cape *et al.* (1991)
Pinus sylvestris L.	28	1520	8	816	68%	2%	Aussenac (1968)
Pinus sylvestris L.	29	2270	6	1637	59%	7%	Cape *et al.* (1991)
Pinus syivestris L.	33	3900	6	918	55%	14%	Cape *et al.* (1991)
Conifers (main species: *Pinus strobus* L.)	–	–	16–25	1046	73%	2%	Neary and Gizyn (1994)
Pinus nigra var. *pallasiana*	48	–	3	1061	65%	4%	Cepel (1967)
Pinus resinosa Ait.	35	1235	7	340	80%	1%	Voigt (1960)
Abies grandis (D. Don) Lindl.	35	620	5	816	57%	1%	Aussenac (1968)
Larix decidua Mill.	33	3900	6	918	77%	4%	Cape *et al.* (1991)
Larix decidua Mill.	27	1600	6	1005	84%	<1%	Cape *et al.* (1991)
Tsuga canadensis (L.) Carr.	–	–	7	340	61%	6%	Voigt (1960)

[a] Sampling of all trees within 15 2 m-diameter plots.
[b] Rainfall depth over the sampled period. Given is the annual average, unless indicated otherwise.
[c] Over 21 months.
[d] This high percentage for stemflow was ascribed to fog, which was collected by stemflow collectors but not by rain gauges.

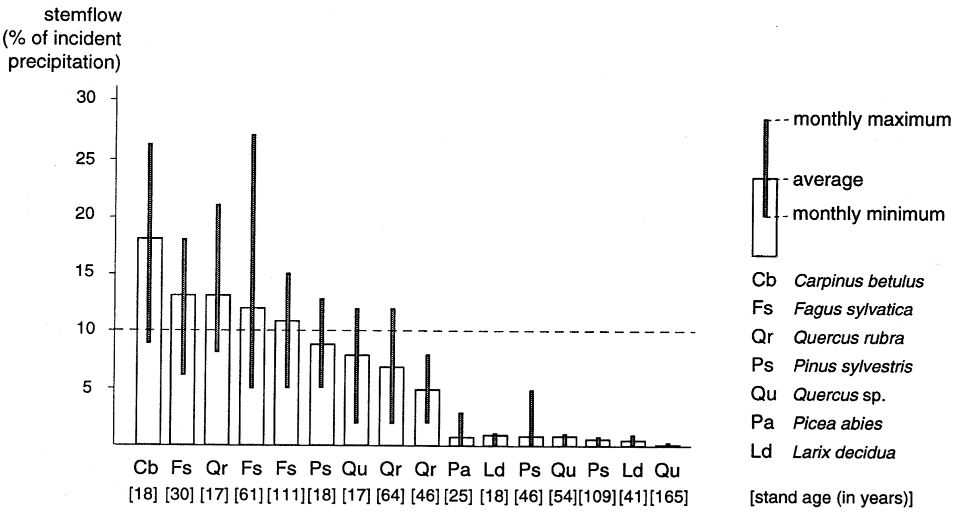

Figure 8. Stemflow in forest stands of different tree species and ages: mean, monthly maximum and minimum in percentage of incident precipitation ($P = 775$ mm) (after Brechtel, 1970, in Brechtel, 1989).

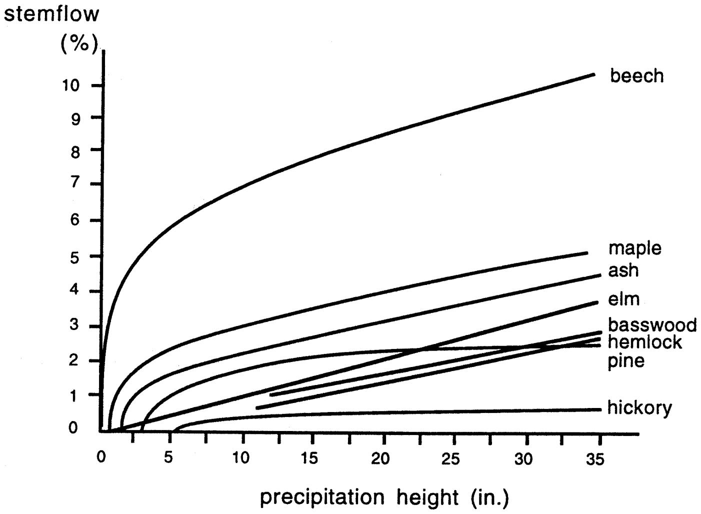

Figure 9. Stemflow as a percentage of precipitation height per storm for different tree genera (after Kittredge, 1948, in Mayer, 1987).

The importance of stemflow can be inferred from the species composition and the age of the stand. Stemflow amount is affected by bark smoothness, stem diameter and branch angle. It is highest for large-crowned emergent trees with smooth bark and upright branches (Parker, 1983). Stemflow volumes are especially high in beech (*Fagus* sp.) forests (e.g. Cepel, 1967; Aussenac, 1968; Brechtel, 1989; Figures 8 and 9; Table III). As the stand grows older, the proportion of stemflow decreases (Johnson, 1990). Greater amounts of stemflow in young stands may be attributed to the higher density of stems (Table III), as well as to the smoother bark of young trees and their tendency for upward branching (Helvey and Patric, 1965). Table III shows examples of stemflow contributions for various species. Further data can be obtained from Helvey and Patric (1965) and Helvey (1971), who synthesised the results of interception studies in hardwood and conifer stands of North America in the form of linear regression equations, in which throughfall and stemflow are presented as functions of incident rainfall. The contribution of stemflow to chemical fluxes may be considerable as stemflow is usually more acidic and more concentrated than throughfall (Parker, 1983), although reactions on the tree trunk can partly remove some nutrients from the solution (Neal *et al.*, 1994). The contribution of stemflow to the total sulphur deposition to the forest floor has been shown to amount to more than 30% in some *Fagus sylvatica* stands (Mayer, 1987).

On the basis of these considerations, monitoring manuals usually require stemflow measurement in *Fagus* sp. stands, and recommend it in other deciduous stands, and young spruce and pine stands (Environmental Data Centre, 1993; Programme Coordinating Centres, 1994). In cases where it is unclear whether stemflow should be measured or not, its contribution should be assessed in a pilot study. Such a pilot study, carried out over a sufficient time, would also enable the determination of the parameters of simple models linking stemflow volume to incident precipitation for the site (e.g. Mayer, 1987; Brechtel, 1989).

4.2.2. *Spatial Variation, Number of Collectors and Siting in the Field*

Spatial variation of stemflow is stronger than that of throughfall (Weihe, 1985; Duijsing *et al.*, 1986; Brechtel, 1989; Loustau *et al.*, 1992). In an homogeneous *Pinus pinaster* plantation, Loustau *et al.* (1992) concluded that more than 40 collectors would be needed to estimate stemflow volumes within 10% of the mean with a 95% confidence level. In beech stands, Weihe (1985) calculated that 30 to 80 collectors were necessary to yield estimates of stemflow volumes with a precision of 10% and a 95% confidence interval. Brechtel (1989) also reported that even in forest stands with high volumes of stemflow, 50 to 100 trees would have to be sampled to obtain a precision of 10% with a level of probability of 90–95%.

Such a high number of collectors is usually not feasible. The ICP-Forests manual (Programme Coordinating Centres, 1994) gives a guideline number of 5 to 10 stemflow gauges; the ICP-Integrated Monitoring manual (Environmental Data Centre, 1993) recommends sampling 10 to 20 trees of the predominant species. The effective number of collectors should be adjusted in relation to the characteristics of the stand. Fewer collectors are required for homogeneous, even-aged stands than for mixed stands with trees of different diameter and canopy size classes. The number of necessary collectors can be reduced by a stratified sampling design based on the number of stems and the basal area, which is correlated to the size of the crown (Parker, 1983; Weihe, 1985). Total stemflow amount can then be extrapolated for the whole plot using the following formula (Programme Coordinating Centres, 1994)

$$\text{total volume in the plot (mm)} = \frac{\text{total stemflow of } n \text{ trees (l)}}{\text{plot area (ha)}} \times$$

$$\frac{\text{total basal area of all trees in the plot}}{\text{total basal area of the } n \text{ trees}} \times 10^{-4}$$

where n is the number of trees used for the stemflow measurements.

4.3. PRECIPITATION IN THE OPEN

Extrapolation of precipitation measurements from one area to another at the regional scale (10–100 km scale) is not recommended, as the influence of local or orogenic features can be significant (e.g. Beier and Rasmussen, 1989; Paturel and Chocat, 1994). Rain collectors should be placed in a nearby open area with the same general site features as the studied forest stand in order to obtain a measurement representative of the incident precipitation for the forest plot. The chosen area should also be free from the influence of local potential sources of emissions of compounds such as roads or agricultural fields (Galloway and Likens, 1978; Bigelow, 1991).

The open area should preferably be wind-shielded (a clearing in a forest with a grass cover provides ideal conditions) (Galloway and Likens, 1978) but also large enough to avoid the precipitation chemistry or amount being influenced by the surrounding objects (trees or buildings). WMO (1971, in EMEP, 1977) recommends that the surrounding objects should not be closer to the gauge than a distance equal to four times their height. Consistently, the international standard for deposition recommends that the angle should be less than 30° and the distance should be more than 5 m (ISO/DIS 4222 in The Working Group for Environmental Monitoring, 1989). In practice, a greater tolerance is accepted; manuals require that the angle from the opening of the collector to the top of the nearby obstacles should not be more than 45° (Bigelow, 1984; The Working Group for Environmental Monitoring, 1989; Environmental Data Centre, 1993; Programme Coordinating Centres, 1994). Attention should also be paid to the direction of prevailing winds when assessing the possible influence of nearby obstacles (Bigelow, 1984). The ICP-Forests manual (Programme Coordinating Centres, 1994) and the instruction manual for the National Atmospheric Deposition Program in the United States (Bigelow, 1984) advise regular cutting of bushes, trees and high grass on the site, within a radius of at least 10 m.

Precipitation is far less variable than throughfall over small spatial scales (e.g. Ford and Deans, 1978; Galloway and Likens, 1978; Levett *et al.*, 1985; Schroder *et al.*, 1985), although significant differences between co-located samplers have been observed for periods with high wind speed or in winter (Beier and Rasmussen, 1989; Nilles *et al.*, 1994), or even in the absence of obvious causes (Crockford *et al.*, 1996). Precipitation should be collected by at least two parallel gauges, thus reducing the risks of loss of samples due to contamination and providing a sufficient amount of solution for analysis in drier periods (The Working Group for Environmental Monitoring, 1989; Programme Coordinating Centres, 1994). The use of a higher number of collectors also reduces the uncertainty in deposition measurement, allowing a more sensitive detection of temporal trends (Slanina *et al.*, 1990). A sufficient distance between the different instruments on the site should be maintained. The instruction manual for the National Atmospheric Deposition Program in the United States recommends that any object over 1 m high with sufficient mass to deflect wind should not be located within 5 m of the collector (installed on a 1 m high base) (Bigelow, 1984). Violation of these criteria had a significant influence on the catch efficiency of the collectors (Graham, 1990).

5. Conclusion

Although less complex than the measurement of the dry or occult components of atmospheric deposition, dependable quantification of element fluxes under forest canopies raises many problems, primarily due to the strong spatial and temporal variability of throughfall and stemflow. Generalisation of the results of the few studies which have addressed this issue is difficult. Studies are generally undertaken with specific sampling designs and time and space conditions, leading to contradictory results. This may explain the lack of general agreement over sampling methods, and the inconsistencies between the recommendations of different monitoring programmes. As a result, only general guidelines can be proposed.

The most reliable estimates of the water and nutrient fluxes are obtained by covering the whole study plot by a network of collectors which can be placed randomly or systematically as long as the distribution does not overlap any existing pattern. The number of necessary throughfall and stemflow collectors must be inferred from a pilot study specific to the site. When computing the necessary sample size, the rate of improvement of the estimates per additional collector should be taken into consideration, in order to assess the limit to which improvement is worth the cost. Fifteen to thirty throughfall collectors may be sufficient if the aim of the study is to establish annual deposition values. The throughfall collectors can be either troughs or funnels, insofar as a fraction of the canopy large enough (not restricted to very few trees only) is sampled. It is better to have several shorter troughs than one single long trough, as wetting and evaporation losses increase concurrently with the length of the trough. Event-based sampling or one week-collection intervals minimise transformations of the water samples in the field.

Two factors limit the implementation of the ideal sampling design. Throughfall and stemflow measurements may be specifically undertaken to study atmospheric deposition, but these measurements may also be associated with complementary studies aiming at a better understanding of processes at the ecosystem level. The sampling design for throughfall and stemflow must then be carefully integrated into the whole concept to avoid any disturbance of the other measurements, and the placement of the collectors is necessarily restricted to one or more subplots in the study site. The second limiting factor is logistics. The analysis costs related to the larger numbers of samples resulting from greater numbers of collectors and shorter sampling intervals may be reduced by pooling the samples of the same type together (throughfall, stemflow from the same tree species), in proportion to volumes, over space or time gradients (according to the aims of the study). However, an increase in management and maintenance costs is inevitable. Consequently, the number of collectors must be reduced and the collection interval must be lengthened. Trough-type collectors may then be preferable because their collecting area samples across a larger canopy gradient. Extrapolation to the whole stand is very uncertain if only one or two of these collectors are installed, and the measurements mainly provide relative values in time. If only few collectors can be operated, then relocation of these collectors (after each collection interval at randomly selected intersections of a fixed sampling grid for example) will limit sampling bias. Documentation of the structure of the canopy will provide useful information in case of monitoring studies. Conservation of the water samples in the field is improved by shielding the collection vessel from light and the collection interval can be extended to two weeks, or a maximum of one month. These compromises are unavoidable concessions to the accuracy and precision of the estimates of the water and nutrient fluxes.

Acknowledgements

I am grateful to Erwin Ulrich for helpful discussion, Michèle Kaennel and Martin Spinnler for their help in gathering the relevant literature, and John L. Innes for his review of the manuscript.

References

Atteia, O. and Dambrine, E.: 1993, ‘Dynamique d’éléments traces dans les précipitations sous le couvert de 2 pessières peu polluées de Suisse romande’, *Annales des Sciences forestières* **50**, 445–459.

Attiwil, P. M.: 1966, ‘The chemical composition of rainwater in relation to cycling of nutrients in mature Eucalyptus forest’, *Plant and Soil* **24**, 390–406.

Aussenac, G.: 1968, ‘Interception des précipitations par le couvert forestier’, *Annales des Sciences forestières* **25**, 135–156.

Aussenac, G.: 1970, ‘Action du couvert forestier sur la distribution au sol des précipitations’, *Annales des Sciences forestières* **27**, 383–399.

Bächmann, K., Haag, I. and Röder, A.: 1993, ‘A field study to determine the chemical content of individual raindrops as a function of their size’, *Atmospheric Environment* **27A**, 1951–1958.

Beier, C. and Gundersen, P.: 1989, ‘Atmospheric deposition to the edge of a spruce forest in Denmark’, *Environmental Pollution* **60**, 257–271.

Beier, C., Gundersen, P. and Rasmussen, L.: 1992, 'A new method for estimation of dry deposition of particles based on throughfall measurements in a forest edge', *Atmospheric Environment* **26A**, 1553–1559.

Beier, C., Hansen, K. and Gundersen, P.: 1993, 'Spatial variability of throughfall fluxes in a spruce forest', *Environmental Pollution* **81**, 257–267.

Beier, C. and Rasmussen, L.: 1989, 'Problems related to collection of rain and throughfall water', *Air Pollution Report Series* **21**, 101–110.

Bigelow, D. S.: 1984, *Instruction manual – NADP/NTN site selection and installation*, NADP Coordinator's Office, Colorado State University, Fort Collins, Colorado.

Bigelow, D. S.: 1991, 'Comparability of wet-only precipitation chemistry measurements from the United States' National Atmospheric Deposition Program (NADP) to those of the Canadian Network for Sampling Acid Precipitation (CANSAP)', *Environmental Science and Technology* **25**, 1867–1865.

Bigelow, D. S., Sisterson, D. L. and Schroder, L. J.: 1989, 'An interpretation of differences between field and laboratory pH values reported by the National Atmospheric Deposition Program/National Trends Network Monitoring Program', *Environmental Science and Technology* **23**, 881–887.

Bogen, D. C., Nagourney, S. J. and Torquato, C.: 1980, 'A field evaluation of the HASL wet-dry deposition collector', *Water, Air, and Soil Pollut.* **13**, 453–458.

Brechtel, H. M.: 1970, 'Wald und Retention. Eine einfache Methoden zur Bestimmung der lokalen Bedeutung des Waldes für die Hochwasserdämpfung', *Deutsche Gewässerkundliche Mitteilungen* **4**, 91–103.

Brechtel, H. M.: 1989, 'Monitoring wet deposition in forests. Quantitative and qualitative aspects', *Air Pollution Report Series* **21**, 39–62.

Bredemeier, M.: 1988, 'Forest canopy transformation of atmospheric deposition', *Water, Air, and Soil Pollut.* **40**, 121–138.

Bredemeier, M. and Lindberg, S. E.: 1992, 'Stoffeinträge in Niederschlagsproben. Vergleich zwischen Einzel- und Gesamt(Bulk)-Niederschlagsproben in einem Fichtenwald', *Staub – Reinhaltung der Luft* **52**, 67-72.

Brown, A. D. and Lund, L. J.: 1994, 'Factors controlling throughfall characteristics at a high elevation Sierra Nevada site, California', *J. Environmental Quality* **23**, 844–850.

Burch, H., Waldner, P. and Fritschi, B.: 'Variation of pH and concentration of nutrients and minerals during rain-events', *Proceedings of the 6th conference of Experimental and Representative Basin Network (ERB)*, 1996/09/24–26 Strasbourg, France (in press).

Camuffo, D., Bernardi, A. and Zanetti, M.: 1988, 'Analysis of the real-time measurement of the pH of rainfall at Padova, Italy: seasonal variations and meteorological aspects', *Science of the Total Environment* **71**, 187–200.

Cape, J. N.: 1989, 'Variability within forest in throughfall and stemflow', *Air Pollution Report Series* **21**, 155–161.

Cape, J. N., Brown, A. H. F., Robertson, S. M. C., Howson, G. and Paterson, I. S.: 1991, 'Interspecies comparisons of throughfall and stemflow at three sites in Northern Britain', *Forest Ecology and Management* **46**, 165–177.

Cappellato, R. and Peters, N. E.: 1995, 'Dry deposition and canopy leaching rates in deciduous and coniferous forests of the Georgia Piedmont: an assessment of a regression model', *J. Hydrology* **169**, 131–150.

Carleton, T. J. and Kavanagh, T.: 1990, 'Influence of stand age and spatial location on throughfall chemistry beneath black spruce', *Canadian Journal of Forest Research* **20**, 1917–1925.

Carlisle, A., Brown, A. H. F. and White, E. J.: 1966, 'The organic matter and nutrient elements in the precipitation beneath a sessile oak (*Quercus petraea*) canopy', *J. Ecology* **54**, 87–98.

Carlisle, A., Brown, A. H. F. and White, E. J.: 1967, 'The nutrient content of tree stem flow and ground flora litter and leachates in a sessile oak (*Quercus petraea*) woodland', *J. Ecology* **55**, 615–627.

Cepel, N.: 1967, 'Interzeption (= Niederschlagsverdunstung im Kronenraum) in einem Buchen-, einem Eichen- und einem Kiefernbestand des Belgrader Waldes bei Istanbul', *Forstwissenschaftliches Centralblatt* **86**, 301–314.

Claassen, H. C. and Halm, D. R.: 1995a, 'A possible deficiency in estimates of wet deposition obtained from data generated by the NADP/NTN network', *Atmospheric Environment* **29**, 437–448.

Claassen, H. C. and Halm, D. R.: 1995b, 'Performance characteristics of an automated wet deposition collector and deposition effect on computed annual deposition', *Atmospheric Environment* **29**, 1021–1026.

Crockford, R. H. and Richardson, D. P.: 1990, 'Partitioning of rainfall in a eucalypt forest and pine plantation in southeastern Australia: I Throughfall measurement in a eucalypt forest: effect of method and species composition', *Hydrological Processes* **4**, 131–144.

Crockford, R. H., Richardson, D. P. and Sageman, R.: 1996, 'Chemistry of rainfall, throughfall and stemflow in a eucalypt forest and a pine plantation in south-eastern Australia. 1. Rainfall', *Hydrological Processes* **10**, 1–11.

Czarnowski, M. S. and Olszewski, J. L.: 1970, 'Number and spacing of rainfall gauges in a deciduous forest stand', *Oikos* **21**, 48–51.

Dasch, J. M.: 1985. 'The direct measurement of dry deposition to a polyethylene bucket and various surrogate surfaces', *Environmental Science and Technology* **19**, 721–725.

De Pena, R. G., Pena, J. A. and Bowersox, V. C.: 1980, *Precipitation collectors intercomparison study*, Department of Meteorology, The Pennsylvania State University, University Park, Pennsylvania.

De Pena, R. G., Walker, K. C., Lebowitz, L. and Micka, J. G.: 1985, 'Wet deposition monitoring: effect of sampling period', *Atmospheric Environment* **19**, 151–156.

Draaijers, G. P. J. and Erisman, J. W.: 1993, 'Atmospheric sulphur deposition to forest stands: throughfall estimates compared to estimates from inference', *Atmospheric Environment* **27A**, 43–55.

Draaijers, G. P. J., Erisman, J. W., Spranger, T. and Wyers, G. P.: 1996, 'The application of throughfall measurements for atmospheric deposition monitoring', *Atmospheric Environment* **30**, 3349–3361.

Draaijers, G. P. J., Ivens, W. P. M. F. and Bleuten, W.: 1988, 'Atmospheric deposition in forest edges measured by monitoring canopy throughfall', *Water, Air, and Soil Pollut.* **42**, 129–136.

Draaijers, G. P. J., van Ek, R. and Meijers, R.: 1992, 'Research on the impact of forest stand structure on atmospheric deposition', *Environmental Pollution* **75**, 243–249.

Duijsings, J. J. H. M., Verstraten, J. M. and Bouten, W.: 1986, 'Spatial variability in nutrient deposition under an oak/beech canopy', *Zeitschrift für Pflanzenernährung und Bodenkunde* **149**, 718–727.

Edwards, P. J., Mohai, P., Halverson, H. G. and DeWalle, D. R.: 1989, 'Consideration for throughfall chemistry sample–size determination', *Forest Science* **35**, 173–182.

EMEP: 1977, *Co-operative Programme for Monitoring and Evaluation of the Long Range Transmission of Air Pollutants in Europe. Manual for sampling and chemical analysis*, EMEP/CHEM 3/77, Norwegian Institute for Air Research Lillestrøm, Norway.

Environmental Data Centre (eds.): 1993, *International Co-operative Programme on Integrated Monitoring on Air Pollution Effects: Manual for integrated monitoring. Programme Phase 1993–1996*, Environmental Data Centre (EDC), Helsinki.

Erisman, J. W., Beier, C., Draaijers, G. P. J. and Lindberg, S. E.: 1994, 'Review of deposition monitoring methods', *Tellus* **46B**, 79–93.

Ferm, M.: 1993, 'Throughfall measurements of nitrogen and sulphur compounds', *International Journal of Analytical Chemistry* **50**, 29–43.

Ford, E. D. and Deans, J. D.: 1978, 'The effects of canopy structure on stemflow, throughfall and interception loss in a young Sitka spruce plantation', *J. Applied Ecology* **15**, 905–917.

Freiesleben, N. E. v., Ridder, C. and Rasmussen, L.: 1986, 'Patterns of acid deposition to a Danish spruce forest', *Water, Air, and Soil Pollut.* **30**, 135–141.

Galloway, J. N. and Likens, G. E.: 1976, 'Calibration of collection procedures for the determination of precipitation chemistry', *Water, Air, and Soil Pollut.* **6**, 241–258.

Galloway, J. N. and Likens, G. E.: 1978, 'The collection of precipitation for chemical analysis', *Tellus* **30**, 71–82.

Glaubig, R. and Gomez, A.: 1994, 'A simple, inexpensive rain and canopy throughfall collector', *J. Environmental Quality* **23**, 1103–1107.

Graham, R. C.: 1990, 'An assessment of performance of wet atmospheric deposition samplers. Part 2. Validation of siting criteria', *Water, Air, and Soil Pollut.* **52**, 97–114.

Graham, R. C. and Obal, J.: 1989, 'The non-parametric statistical evaluation of precipitation chemistry sampler intercomparison data', *Atmospheric Environment* **23**, 1117–1130.

Graham, R. C., Robertson, J. K., Schroder, L. and Lafemina, J.: 1988, 'Atmospheric deposition sampler intercomparison', *Water, Air, and Soil Pollut.* **37**, 139–147.

Granat, L.: 1974. 'On the deposition of chemical substances by precipitation', *WMO-report* **368**, 71–78.

Hall, D. J., Irwin, J. G., Stone, B. H. and Upton, S. L.: 1993, 'Aerodynamic Considerations in Precipitation Collector Design', in S. Couling (ed.), *Measurement of Airborne Pollutants*, Butterworth-Heinemann, Oxford, 108–148.

Hansen, K.: 1995, 'In-canopy throughfall measurements in Norway spruce: water flow and consequences for ion fluxes', *Water, Air, and Soil Pollut.* **85**, 2259–2264.

Hansen, K., Draaijers, G. P. J., Ivens, W. P. M. F., Gundersen, P. and van Leeuwen, N. F. M.: 1994, 'Concentration variations in rain and canopy throughfall collected sequentially during individual rain events', *Atmospheric Environment* **28**, 3195–3205.

Hasselrot, B. and Grennfelt, P.: 1987, 'Deposition of air pollutants in a wind-exposed forest edge', *Water, Air, and Soil Pollut.* **34**, 135–143.

Helvey, J. D.: 1971, 'A Summary of Rainfall Interception by Certain Conifers of North America', in E. J. Monke (ed.), *Biological Effects in the Hydrological Cycle-Terrestrial Phase*, Experiment Station, West Lafayette, IN, 103–113.

Helvey, J. D. and Patric, J. H.: 1965, 'Canopy and litter interception of rainfall by hardwoods of Eastern United States', *Water Resources Research* **1**, 193–206.

Hogg, S. E., Murray, D. L. and Manly, B. F. J.: 1977, 'Methods of estimating throughfall under a forest', Paper presented at Annual Symposium throughfall of the New Zealand Hydrological Society.

Huff, F. A.: 1955, 'Comparison between standard and small orifice rain gages', *Transactions of the American Geophysical Union* **36**, 689–694.

Johnson, R. C.: 1990, 'The interception, throughfall and stemflow in a forest in highland Scotland and the comparison with other upland forests in the U.K.' *J. Hydrology* **118**, 281–287.

Johnson, D. W., Richter, D. D., Lovett, G. M. and Lindberg, S. E.: 1985, 'The effects of atmospheric deposition on potassium, calcium, and magnesium cycling in two deciduous forests', *Canadian Journal of Forest Research* **15**, 773–782.

Johnson, D. W. and Lindberg, S. E. (eds.): 1992, *Atmospheric Deposition and Forest Nutrient Cycling: A Synthesis of the Integrated Forest Study*, Ecological studies 91, New York, Springer.

Joslin, J. D. and Wolfe, M. H.: 1992, 'Tests of the use of net throughfall sulfate to estimate dry and occult sulfur deposition', *Atmospheric Environment* **26A**, 63–72.

Keene, W. C. and Galloway, J. N.: 1984, 'Organic acidity in precipitation of North America', *Atmospheric Environment* **18**, 2491–2497.

Kimmins, J. P.: 1973, 'Some statistical aspects of sampling throughfall precipitation in nutrient cycling studies in British Columbian coastal forests', *Ecology* **54**, 1008–1019.

Kittredge, J.: 1948, *Forest Influences*, New York, McGraw Hill Book Co.

Kostelnik, K. M., Lynch, J. A., Grimm, J. W. and Corbett, E. S.: 1989, 'Sample size requirements for estimation of throughfall chemistry beneath a mixed hardwood forest', *J. Environmental Quality* **18**, 274–280.

Lawrence, G. B. and Fernandez, I. J.: 1993, 'A reassessment of areal variability of throughfall deposition measurements', *Ecological Applications* **3**, 473–480.

Levett, M. P., Adams, J. A. and Walker, T. W.: 1985, 'Sampling variability in nutrient cycling studies in some forested ecosystems of Westland, New Zealand', *New Zealand Journal of Botany* **23**, 407–415.

Lewis, W. M. Jr. and Grant, M. C.: 1978, 'Sampling and chemical interpretation of precipitation for mass balance studies', *Water Resources Research* **14**, 1098–1104.

Liechty, H. O. and Mroz, G. D.: 1991, 'Effects of collection interval on quality of throughfall samples in two northern hardwood stands', *J. Environmental Quality* **20**, 588–590.

Lloyd, C. R. and Marques, A. de O.: 1988, 'Spatial variability of throughfall and stemflow measurements in Amazonian rainforest', *Agricultural and Forest Meteorology* **42**, 63–73.

Loustau, D., Berbigier, P., Granier, A. and El Hadj Moussa, F.: 1992, 'Interception loss, throughfall and stemflow in a maritime pine stand. I. Variability of throughfall and stemflow beneath the pine canopy', *J. Hydrology* **138**, 449–467.

Lovett, G. M. and Lindberg, S. E.: 1984, 'Dry deposition and canopy exchange in a mixed oak forest as determined by analysis of throughfall', *J. Applied Ecology* **21**, 1013–1027.

Madsen, B. C.: 1982, 'An evaluation of sampling interval length on the chemical composition of wet–only deposition', *Atmospheric Environment* **16**, 2515–2519.

Matzner, E. and Meiwes, K. J.: 1994, 'Long–term development of element fluxes with bulk precipitation and throughfall in two German forests', *J. Environmental Quality* **23**, 162–166.

Mayer, R.: 1987, 'Throughfall and stemflow mechanisms: Deposition pattern of air pollutants below vegetation cover', *Air Pollution Research Report* **6**, 96–106.

Meesenburg, H., Meiwes, K. J. and Rademacher, P.: 1995, 'Long term trends in atmospheric deposition and seepage output in northwest German forest ecosystems', *Water, Air, and Soil Pollut.* **85,** 611–616.

Minoura, H. and Iwasaka, Y.: 1996, 'Rapid change in nitrate and sulfate concentrations observed in early stage of precipitation and their deposition processes', *J. Atmospheric Chemistry* **24**, 39–55.

Mosello, R., Marchetto, A. and Tartari, G. A.: 1988, 'Bulk and wet atmospheric deposition chemistry at Pallanza (N. Italy)', *Water, Air, and Soil Pollut.* **42**, 137–151.

Müller, K. P., Aheimer, G. and Gravenhorst, G.: 1982, 'The Influence of Immediate Freezing on the Chemical Composition of Rain Sample', in H. W. Georgii and J. Pankrath (eds.), *Deposition of Atmospheric Pollutants*, Dordrecht, Reidel, 125–132.

Neal, C., Ryland, G. P., Conway, T., Jeffery, H. A., Neal, M., Robson, A. J., Smith, C. J., Walls, J. and Bhardwaj, C. L.: 1994, 'Interception of chemicals at a forest edge for a rural low–lying site at Black Wood, Hampshire, southern England', *Science of the Total Environment* **142**, 127–141.

Neary, A. J. and Gizyn, W. I.: 1994, 'Throughfall and stemflow chemistry under deciduous and coniferous forest canopies in south-central Ontario', *Canadian Journal of Forest Research* **24**, 1089–1100.

Nihlgård, B: 1970, 'Precipitation, its chemical composition and effect on soil water in a beech and spruce forest in south Sweden', *Oikos* **21**, 208–217.

Nilles, M. A., Gordon, J. D. and Schroder, L. J.: 1994, 'The precision of wet atmospheric deposition data from National Atmospheric Deposition Program National Trends Network sites determined with collocated samplers', *Atmospheric Environment* **28**, 1121–1128.

Nordén, U.: 1991, 'Acid deposition and throughfall fluxes of elements as related to tree species in deciduous forests of south Sweden', *Water, Air, and Soil Pollut.* **60**, 209–230.

Parker, G. G.: 1983, 'Throughfall and stemflow in the forest nutrient cycle', *Advances in Ecological Research* **13**, 58–135.

Paturel, J. E. and Chocat, B.: 1994, 'Analysis of the rain phenomenon at fine spatial scale', *Water Science and Technology* **29**, 31–37.

Peden, J. L.: 1988, *Quality assurance report: NADP/NTN deposition monitoring, laboratory operations, central analytical laboratory, 1984 through 1985*, National Atmospheric Deposition Program, Natural Resource Ecology Laboratory, Colorado State University, Ft. Collins, CO.

Peden, M. and Skowron, L.: 1978, 'Ionic stability of precipitation samples', *Atmospheric Environment* **12**, 2343–2349.

Pedersen, L. B.: 1992, 'Throughfall chemistry of Sitka spruce stands as influenced by tree spacing', *Scandinavian Journal of Forest Research* **7**, 433–444.

Peterson, D. L. and Rolfe, G. L.: 1979, 'Determining sample size in throughfall studies', *Forest Science* **25**, 582–584.

Potter, C. S., Ragsdale, H. L. and Swank, W. T.: 1991, 'Atmospheric deposition and foliar leaching in a regenerating Southern Appalachian forest canopy', *J. Ecology* **79**, 97–115.

Programme Coordinating Centres (eds.): 1994, *International Co-operative Programme on Assessment and Monitoring of Air Pollution Effects on Forests: Manual on methods and criteria for harmonized sampling, assessment, monitoring and analysis of the effects of air pollution on forests*, Programme Coordinating Centres, Hamburg, Prague.

Puckett, L. J.: 1990, 'Estimates of ion sources in deciduous and coniferous throughfall', *Atmospheric Environment* **24A**, 545–555.

Puckett, L. J.: 1991, 'Spatial variability and collector requirements for sampling throughfall volume and chemistry under a mixed-hardwood canopy', *Canadian Journal of Forest Research* **21**, 1581–1588.

Rasmussen, L. and Beier, C.: 1987, 'Improved methods for throughfall and stemflow collection', *Air Pollution Research Report* **4**, 92–97.

Reigner, I. C.: 1964, *Evaluation of the trough-type rain gage, U.S. Forest Service Northeastern Forest Experiment Station Research Note 20.*

Reynolds, R.: 1996, 'Estimating the total deposition of base cations from throughfall measurements', *Science of the Total Environment* **180**, 183–186.

Reynolds, B., Cape, J. N. and Paterson, I. S.: 1989, 'A comparison of element fluxes in throughfall beneath larch and Sitka spruce at two contrasting sites in the United Kingdom', *Forestry* **62**, 29–39.

Reynolds, E. R. C. and Leyton, L.: 1963, 'Measurement and Significance of Throughfall in Forest Stands', in A. J. Rutter and F. H. Whitehead (eds.), *Water Relations of Plants*, Oxford, Blackwell Scientific Publications, 127–141.

Reynolds, B. and Neal, C.: 1991, 'Trough versus funnel collectors for measuring throughfall volumes', *J. Environmental Quality* **20**, 518–521.

Richter, D. D. and Lindberg, S. E.: 1988, 'Wet deposition estimates from long-term bulk and event wet-only samples of incident precipitation and throughfall', *J. Environmental Quality* **17**, 619–622.

Robson, A. J., Neal, C., Ryland, G. P. and Harrow, M.: 1994, 'Spatial variations in throughfall chemistry at the small plot scale', *J. Hydrology* **158**, 107–122.

Rodda, J. C. and Smith, S. W.: 1986, 'The significance of the systematic error in rainfall measurement for assessing wet deposition', *Atmospheric Environment* **20**, 1059–1064.

Rodda, J. C., Smith, S. W. and Strangeways, I. C.: 1985, 'On more realistic measurements of rainfall and their impact on assessing acid deposition', *Zürcher Geographische Schriften* **23**, 245–249.

Rustad, L. E., Kahl, J. S., Norton, S. A. and Fernandez, I. J.: 1994, 'Underestimation of dry deposition by throughfall in mixed northern hardwood forests', *J. Hydrology* **162**, 319–336.

Schroder, L. J., Linthurst, R. A., Ellson, J. E. and Vozzo, S. F.: 1985, 'Comparison of daily and weekly precipitation sampling efficiencies using automatic collectors', *Water, Air, and Soil Pollut.* **24**, 177–188.

Seiler, J. and Matzner, E.: 1995, 'Spatial variability of throughfall chemistry and selected soil properties as influenced by stem distance in a mature Norway spruce (*Picea abies*, Karst.) stand', *Plant and Soil* **176**, 139–147.

Sevruk, B.: 1989, 'Reliability of Precipitation Measurement', in B. Sevruk (ed.), *Precipitation Measurement*, Swiss Federal Institute of Technology (ETH), Zürich, 13–19.

Sevruk, B., Hertig, J. A. and Tettamanti, R.: 1994, 'The effect of orifice rim thickness on the wind speed above precipitation gauges', *Atmospheric Environment* **28**, 1939–1944.

Sisterson, D. L., Wurfel, B. E. and Lesht, B. M.: 1985, 'Chemical differences between event and weekly precipitation samples in Northeastern Illinois', *Atmospheric Environment* **19**, 1453–1469.

Slanina, J.: 1983, 'Collection and analysis of precipitation, methods, data evaluation and interpretation', *VDI-Berichte* **500**, 117–124.

Slanina, J.: 1986, 'Standardized Techniques for the Collection and Analysis of Precipitation', in W. Jaeschke (ed.), *Chemistry of Multiphase Atmospheric Systems*, Berlin, Springer-Verlag, 91–115.

Slanina, J., Baard, J. H., Broersen, B. C., Möls, J. J. and Voors, P. I.: 1987, 'The stability of precipitation samples under field conditions', *International Journal of Environmental Analytical Chemistry* **28**, 247–261.

Slanina, J., Möls, J. J. and Baard, J. H.: 1990, 'The influence of outliers on results of wet deposition measurements as a function of measurement strategy', *Atmospheric Environment* **24A**, 1843–1860.

Slanina, J., Möls, J. J., Baard, J. H., van der Sloot, H. A., van Raaphorst, J. G. and Asman, W. A. H.: 1979, 'Collection and analysis of rainwater; experimental problems and the interpretation of results', *International Journal of Environmental Analytical Chemistry* **7**, 161–176.

Soederlund, R. and Granat, L.: 1982, 'On the difference in chemical composition of precipitation collected in bulk and wet-only collectors', *Report CM-57*, Department of Meteorology, University of Stockholm.

Stedman, J. R., Heyes, C. J. and Irwin, J. G.: 1990, 'A comparison of bulk and wet-only precipitation collectors at rural sites in the United Kingdom', *Water, Air, and Soil Pollut.* **52**, 377–395.

Stout, B. B. and McMahon, R. J.: 1961, 'Throughfall variation under tree crowns', *J. Geophysical Research* **66**, 1839–1843.

Stuart, G. W.: 1962, *A study of rainfall interception by an oak-hickory forest cover on a watershed in central Pennsylvania*, M.S. Thesis, Pennsylvania State University.

Tang, A. J. S., Chan, W. H., Orr, D. B., Bardswick, W. S., and Lusis, M. A.: 1987, 'An evaluation of the precision, and various sources of error, in daily and cumulative precipitation chemistry sampling', *Water, Air, and Soil Pollut.* **36**, 91–102.

The Working Group for Environmental Monitoring – Nordic Council of Ministers (eds.): 1989, *Methods for Integrated Monitoring in the Nordic Countries, Miljørapport 1989:11.*

Thimonier, A.: 1994, *Changements de la végétation et des sols en forêt tempérée européenne au cours de la période 1970–1990: rôle possible des apports atmosphériques*, Ph.D. Thesis, Paris XI University/INRA-Nancy.

Ulrich, B.: 1983, 'Interaction of Forest Canopies with Atmospheric Constituents: SO_2, Alkali and Earth Alkali Cations and Chloride', in B. Ulrich and J. Pankrath (eds.), *Effects of Accumulation of Air Pollutants in Forest Ecosystems*, Reidel, Dordrecht, 33–45.

Ulrich, E. and Lanier, M.: 1993, *RENECOFOR – Manuel de référence no. 3 pour le fonctionnement du sous-réseau CATAENAT. Placettes de niveau 2 et 3 (Level III plots within the European Community)*, Deuxième version, Office National des Forêts – Département des Recherches Techniques, Fontainebleau.

Ulrich, E., Lelong, N., Lanier, M. and Schneider, A.: 1995, 'Interception des pluies en forêt: facteurs déterminants. Interprétation des mesures réalisées dans le sous-réseau CATAENAT de RENECOFOR', *ONF – Bulletin Technique* **30**, 33–44.

Van der Maas, M. P. and Valent, A.: 1989, '*In situ* conservation of throughfall samples', *Air Pollution Report Series* **21**, 137.

Van Ek, R. and Draaijers, G. P. J.: 1994, 'Estimates of atmospheric deposition and canopy exchange for three common tree species in the Netherlands', *Water, Air, and Soil Pollut.* **73**, 61–82.

Voigt, G. K.: 1960, 'Distribution of rainfall under forest stands', *Forest Science* **6**, 2–10.

Weihe, J.: 1976, 'Benetzung und Interzeption von Buchen- und Fichtenbeständen in NW. III. Die Regenmessung im Wald', *Allgemeine Forst- und Jagdzeitung* **147**, 235–240.

Weihe, J.: 1985, 'Benetzung und Interzeption von Buchen- und Fichtenbeständen. V. Die Verteilung des Regens unter Buchenkronen', *Allgemeine Forst- und Jagdzeitung* **156**, 81–89.

Wilm, H. G.: 1943, 'Determining net rainfall under a conifer forest', *J. Agricultural Research* **67**, 501–513.

WMO: 1971, *Guide to meteorological instrument and observing practices*, WMO-No. 8.TP.3, Geneva.