Biogeochemistry **69:** 19–35, 2004.

High temporal resolution of ion fluxes in semi-natural ecosystems – gain of information or waste of resources?

C. ALEWELL[1,*], G. LISCHEID[1], U. HELL[1] and B. MANDERSCHEID[2]
*[1]BITÖK, University of Bayreuth, Bayreuth, D-95440, Germany; [2]ZADI, Information Centre for Genetic Resources (IGR), Bonn, D-53177, Germany; *Author for correspondence (e-mail: christine.alewell@bitoek.uni-bayreuth.de; phone: 49-921-555741; fax: 49-921-555799)*

Received 25 March 2002; accepted in revised form 10 February 2003

Key words: Catchment monitoring, Flux calculation, Heterogeneity, High temporal resolution

Abstract. Monitoring programs of ion concentrations and fluxes in semi-natural ecosystems are confronted with the task to gain as much information as possible with simultaneously minimizing costs and efforts. The aim of this study was (i) to assess how much of the heterogeneity of solution concentrations is lost because of temporal integration of measurements and (ii) to estimate the error in ion fluxes due to temporal integration. High resolution measurements (daily interval) of ion concentrations (sulfate, nitrate, chloride, pH and EC) in throughfall, soil solutions and runoff at the catchment *Lehstenbach* (Fichtelgebirge, Northeast Bavaria, Germany) were compared over a two year period with the reference monitoring program (biweekly measurement interval). Evaluation of the maximum temporal heterogeneity of ion concentrations in throughfall, soil solution and runoff (expressed as minimum, maximum, median and 25–75% percentile) did not result in an overall higher heterogeneity of the high resolution measurements compared to the reference program. The calculation of runoff fluxes from the reference data (biweekly concentration) resulted in significant errors of up to 25% for time periods < 1 year (high resolution data was considered the ″true″ value and set as 100%). However, errors became minor (< 10%) if longer time periods were considered. The suitability of different interpolation methods to up-scale biweekly concentration data for the calculation of runoff fluxes was evaluated in this study. We concluded for the monitoring programs at the *Lehstenbach* catchment that a biweekly measurement interval seemed to be suitable to capture the heterogeneity of ion concentrations and fluxes (and thus temporal trends). In comparison, high resolution measurements with a daily measurement interval were higher in cost, work and time resources and had a relatively low information gain. While the introduced methods are applicable in all monitoring programs, conclusions on temporal resolution of measurements are most likely not valid for systems where ion concentrations have a low autocorrelation length (e.g., agricultural or urban systems with nitrate or pesticide treatment; tropical systems with extreme temperature or hydrological events).

Introduction

Monitoring programs of ion concentrations and fluxes in semi-natural ecosystems are confronted with the task of answering numerous questions. The term ″semi-natural ecosystem″ is used here to differentiate between ecosystems with a relatively low management impact (e.g., forest and grasslands) and agricultural or urban systems.

By evaluating concentrations in and fluxes between the atmosphere, the pedosphere and the hydrosphere, conclusions on ecosystem processes or on cause/effect relationships are drawn by indirect evidence. Because of the high temporal and spatial heterogeneity in deposition parameters, stand structure, soil chemistry and water regime, the determination of ion fluxes and concentrations in precipitation, soil solution and runoff is connected to high errors (Manderscheid and Matzner 1995). Monitoring programs aim at measuring representative values for whole ecosystems. The question arises if the information strived for is really gained. Simultaneously, programs are forced to minimize efforts in costs and resources during times of restricted public monetary resources.

A typical setup of monitoring stations for ion concentrations and fluxes in seminatural ecosystems is illustrated in Figure 1 (BML 1997; Likens and Bormann 1995; Butler and Likens 1998; de Vries et al. 2001; Draaijers et al. 2001). Input with precipitation (either as bulk precipitation or canopy throughfall) is measured as a flux equivalent with bulk samplers that integrate over time (either weekly, biweekly or monthly). Spatial integration of precipitation measurement is very small. For the sake of simplicity, it will be defined here as a ″point″ measurement compared to the ″plot″ or ″catchment″ scale. Soil solution sampling is also integrating over time similarly to precipitation measurements, but in case of suction sampling this is an integration over undefined space. Furthermore, soil solution sampling cannot be regarded as truly flux equivalent because sampled volumes are not equivalent to water fluxes. Thus, water fluxes in the soil are usually modeled values. Runoff measurements are typically done as grab samples from the stream. Thus, runoff can be considered temporally as a ″point″ measurement but is spatially integrating over the whole catchment.

With the above described setup the following errors are to be expected: short-term heterogeneity will most likely be underestimated in precipitation and soil solution because of bulk sampling over time. In contrast, ion fluxes in runoff might be associated to high errors because temporal point measurements might not be representative of total output fluxes. When calculating runoff fluxes the continuous water flow measurement has to be set against concentrations of point measurements at biweekly intervals. Thus, concentration data have to be up-scaled in time, e.g., by interpolation. The question of the right interpolation method is tightly connected to statistical properties of the time series. The higher the autocorrelation, and the less the short-term variance, the smaller the error of an interpolation is likely to be.

Measurement strategies of national and international monitoring programs vary between countries and within countries (Draaijers et al. 2001). The optimal sampling strategy depends, of course, on the measurement aim (e.g., ion fluxes, time series analysis, calibrating a given model, etc.). In many cases, the evaluation of monitoring data has the following objectives: (i) the assessment of frequency distributions and heterogeneity in solutions (e.g., peak concentrations of acidity, trends in solute concentrations) as the solutions are the direct environment for all organisms (e.g., plant roots in soil solution, biota in soils or streams) and (ii) calculation of ion fluxes and budgets to describe or become aware of critical ecosystem states like nutrient losses, acidification of soils and waters or nitrogen saturation (Ulrich

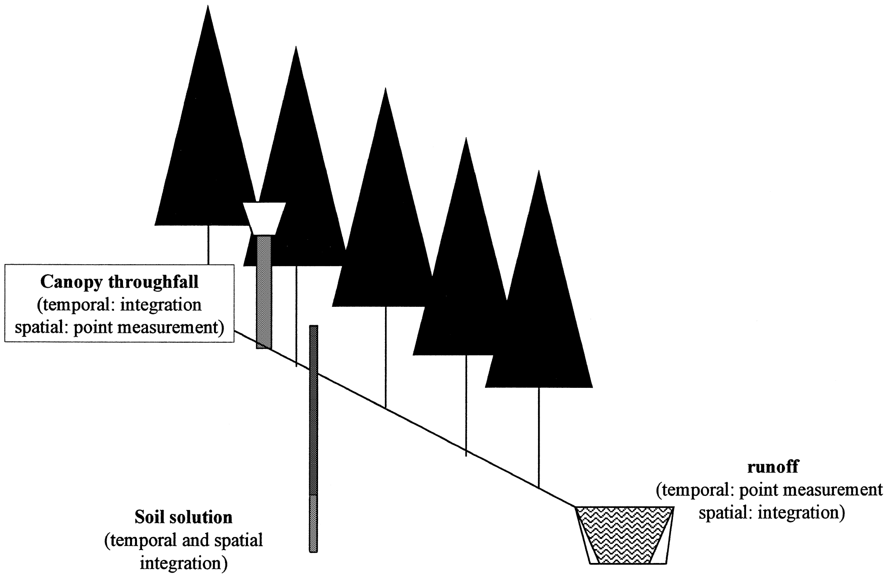

Figure 1. Setup of a typical measurement station for monitoring solution concentrations and ion fluxes in semi-natural ecosystems.

1989; BML 1997; Kleemola and Forsius 1997; Stoddard et al. 1999; de Vries et al. 2001).

Numerous studies have investigated the influence of spatial interpolation of data especially on rainfall patterns (e.g., Dirks et al. 1998; Stow and Dirks 1998). Previous studies done in the catchment *Lehstenbach* (Fichtelgebirge, Northeast Bavaria, Germany) indicated a large spatial heterogeneity in concentrations and fluxes of precipitation and soil solution (Manderscheid and Matzner 1995; Seiler and Matzner 1995; Lischeid et al. 1998). High temporal resolution of measurements has been done in other catchments and has been proven a useful tool in providing information about the short-term dynamics of processes especially during snow melt periods (Laudon 1999; Jenkins et al. 1993; Lischeid et al. 2002) or the determination of travel times (Larocque et al. 1998; Solo-Gabriele 1998). The aims of this study were to assess:

1. How much of the heterogeneity in solution concentrations is lost because of the temporal integration of measurements? How closely is the frequency distribution of the highly resolved data captured by temporally integrating measurements? Do we actually capture solute concentration maxima that could be harmful to flora (e.g., plant roots in the soil) and fauna (e.g., fish or macroinvertebrates in the streams)?
2. Is there a significant increase in the error of the ion fluxes with runoff because of the non-flux equivalent integration over 14 days?

3. Which interpolation method is suitable to up-scale biweekly concentration data for the calculation of runoff fluxes?

Methods

Site

The *Lehstenbach* watershed (4.2 km^2, 50°09′ N, 11°52′ E) is located in the *Fichtelgebirge* area in Northern Bavaria/Germany close to the border with the Czech Republic at an altitude of 695–875 m a.s.l. The granite bedrock weathered deeply during the Tertiary (up to 30 m depth). The average precipitation in the area was appr. 1000 mm and the annual average temperature was 6 °C for the 1988–1999 period. The soils in the upland part of the catchment are acidic and have been classified as dystric Cambisols and Podzols according to the FAO-classification system. 30% of the catchment are covered by boggy areas where soils have been classified as fibric Histosols and dystric Gleysols. 90% of the catchment is stocked with Norway spruce (*Picea abies* (L.) Karst.) of various age classes.

Measurements

Reference samples in this study were taken as part of a long-term monitoring program (1987 to present) at the *Lehstenbach* catchment. Five throughfall collectors (called TF1 to TF5, area = 326 cm^2) were sampled as biweekly bulk samples. Samplers were implemented along a row with 2 m distance. Soil solutions were collected monthly as biweekly bulk samples at 90 cm soil depth using ceramic tension lysimeters. Five replicate lysimeters (Lys1 to Lys5) were established, each located adjacent to a throughfall sampler (distance between lysimeters was 2 m). The reference runoff sampling was simulated from the daily measurements (see below), with every 7th, 14th and 28th sample being considered to simulate weekly, biweekly and monthly sampling.

High resolution measurements were carried out between April 1998 and April 2000. Daily bulk samples (n = 1) of canopy throughfall, soil solution and runoff were collected. The opening of the throughfall collector was 5541,8 cm^2, and solution was collected in a different bottle each day. Soil solution was gained with a suction lysimeter in 90 cm depth as a daily bulk sample. While the throughfall collector was implemented adjacent to the monitoring setup (approximately 3–5 m away from samplers TF1 to TF5), the high resolution lysimeter was implemented within the row of reference lysimeters (approximately 0.5 to 2.5 m away from samplers Lys1 to Lys5). For sampling of the runoff, 10 ml of stream water was pumped at 2-hour intervals and collected as daily bulk samples. All bottles of the high resolution measurement were collected parallel to the reference samples at biweekly intervals.

Water samples were filtered (0.45 µm) and stored at 2 °C before analysis. After filtration, anions (Cl^-, NO_3^-, and SO_4^{2-}) were determined by ion chromatography. The pH was measured with a glass electrode.

Calculation of ion fluxes

Input fluxes with throughfall were calculated as concentration times precipitation amount.

For runoff fluxes of the high resolution measurements, daily water flux was multiplied with daily concentration values. Flux calculations of reference samples were done with the biweekly samples (results regarding the information loss by switching from daily to biweekly measured fluxes should include a change from daily to weekly or weekly to biweekly. Statistically sound evaluations of monthly data were not possible because of the low numbers of observations in a two year period). Continuous water flow measurement had to be combined with concentrations measured at biweekly intervals. Three commonly used calculation procedures were done and we introduce a fourth method. The first method will be referred to as ″weighted interpolation method″. Here, ion flux determined for single days at biweekly intervals were considered as independent samples of a parent population. This is the most pessimistic approach because neither autocorrelation of solute concentration nor correlation between solute concentration and discharge is assumed. It was calculated according to:

$$Q_{weighted} = \sum_i Q_i = \sum_s (q_s \times c_s) \times \frac{\sum_i q_i}{\sum_s q_s}$$

where Q is the calculated ion flux, q the water flux, c solute concentration, s is the index for the sampling days, and i the index for all days of a given period.

The second calculation will be referred to as ″stationary interpolation method″. It is a pragmatic approach, approximating the unobserved solute concentration before a sampling day by considering the one observed at the sampling day, following the formula:

$$Q_{stat} = \sum_{i=s}^{s+1} Q_i = c_{s+1} \times \sum_{i=s}^{s+1} q_i$$

with the subscripts s and $s + 1$ denoting two subsequent samples.

The third method is the linear interpolation method, were daily concentration values are gained by linear interpolation between two measurement points:

$$\hat{c}_{\mathrm{int}} = c_s + (d_i - d_s) \times \frac{c_{s+1} - c_s}{d_{s+1} - d_s} = c_s + (d_i - d_s) \times \frac{\Delta c}{\Delta d}$$

where ĉ is the interpolated concentration, and d is day with $d_s \leqslant d_i \leqslant d_{s+1}$. Fluxes ($Q_{\text{int}}$) can then be calculated as daily concentrations times daily water fluxes.

Method two and three rely on the implicit assumption that autocorrelation of the solute concentration data explains a substantial fraction of the variance of solute concentration between two subsequent sampling days. However, usually autocorrelation decreases with increasing lag length. Thus, the prediction error is likely to increase with increasing distance from the observed values. For very large time lags, the mean value of a stationary time series is then the most probable prediction value. This is explicitly taken into account by our fourth method, an autoregressive model of order one. We applied the autoregressive model as the most theoretically sound way of interpolating between subsequent sampling days. Prior to fitting the autoregressive model, the data were normalized by subtracting the mean, and by subtracting the contribution of the 365 days period, determined by Fourier analysis. This component explained 5%, 64% and 33% of the variance of the daily chloride, nitrate and sulfate concentration data, respectively. Normalized solute concentration at non-sampling days is then calculated by the mean of the autoregressive models based on the preceding and the following sampling day, respectively and weighted according to the distance from these two sampling days:

$$\hat{c}_{n,i} = \frac{d_i - d_s}{d_{s+1} - d_s} \times a^{(d_i - d_s)} c_{n,s} + \frac{d_{s+1} - d_i}{d_{s+1} - d_s} \times a^{(d_{s+1} - d_i)} c_{n,s+1}$$

where c_n is the normalized concentration, and a is the partial autocorrelation for the time lag of 1 day of the normalized time series. For flux calculations (Q_{AR}), the calculated normalized daily solute concentration data were again de-normalized and multiplied with daily water fluxes.

For the calculation of flux errors, cumulative fluxes for the considered periods of the reference sampling calculated with either method were set against the daily measurements. Daily measured fluxes were assumed to be the ″true″ value and were set as 100% values.

Statistical analysis

All data were analyzed with the software package *Statistica '99 Edition*. The test for normal distribution was done with Kolmogorov-Smirnov and normality was rejected if $p < 0.05$. The time series of concentration in precipitation, soil solution and stream water were not normally distributed. Thus, for average values the median was calculated and significant differences were estimated with the non parametric Mann-Whitney-U-Test. The threshold for autocorrelation was defined with a significance level $p < 0.05$.

Removing the seasonal component (Fourier analysis) in runoff time series as well as the fitting of the ARIMA model were done with the software package *SPSS version 6.1*.

Results and discussion

Assessment of heterogeneity

Throughfall and soil solution measurements of the high resolution measurements (one point in space, daily measurement interval) were compared to (i) temporal heterogeneity (minima, maxima, 25–75% percentiles and median) of time series of samplers TF1 to TF5 and Lys1 to Lys5 of the reference measurements and (ii) to the observations from all five samplers representing the maximum heterogeneity of five measurement points in time and space (TF1-5, Lys1-5; Figures 2 and 3). In case of throughfall measurements, the time series with daily measurements resulted in clearly higher maxima than the reference time series with biweekly measurement interval (Figure 2). However, when 25–75% percentiles were compared, there was no clear difference in heterogeneity between daily measurement resolution and reference samples. Furthermore, the medians of concentrations were very similar. Only the median of pH was significantly different between daily measurement (TF) and the reference sampling (TF1-5). Our results are in agreement with Butler and Likens (1998) who compared weekly aggregated with daily precipitation records (1992–1995) at four collocated sites in the eastern USA. Generally, temporal trends of ions were comparable with the exception of problems like loss of NH_4^+ during residence time in the field or differences in base cations due to some differences in filters between measuring programs (Butler and Likens 1998). While the latter is a problem of comparability of different measuring programs, the loss of NH_4^+ due to microbial turnover (and the same would apply to DON, DOC) is a problem which might be solved through, e.g., AgCl application in the samplers but is beyond the scope of this paper.

Regarding soil solution concentrations, high resolution measurements resulted in higher maximum and minimum values in case of chloride and sulfate. Nitrate, pH and electrical conductivity had a higher heterogeneity for either one of the five reference samplers or for the observations from all five samplers together (Lys1-5; Figure 3). Thus, spatial heterogeneity of soil solution concentrations clearly exceeded temporal heterogeneity. Median of SO_4^{2-} concentrations, pH, and electrical conductivity were significantly different between daily measurement (Lys) and the reference sampling (Lys1-5). However, differences were very small compared to the overall heterogeneity.

Time series of the daily runoff measurements (and in case of SO_4^{2-} the weekly measurements) resulted in a slightly higher temporal heterogeneity with lower minima or higher maxima than reference samples. However, the 25–75 percentiles as well as median concentrations were very similar with no significant differences (Figure 4). Most monitoring programs, including the program investigated in this study, collect biweekly or monthly grab samples in the stream. With no integration over time in the sampling strategy of the reference samples, there is only a difference in measurement interval between the high resolution measurements (daily) and the reference (biweekly). Thus, it is only a question of observation numbers to cap-

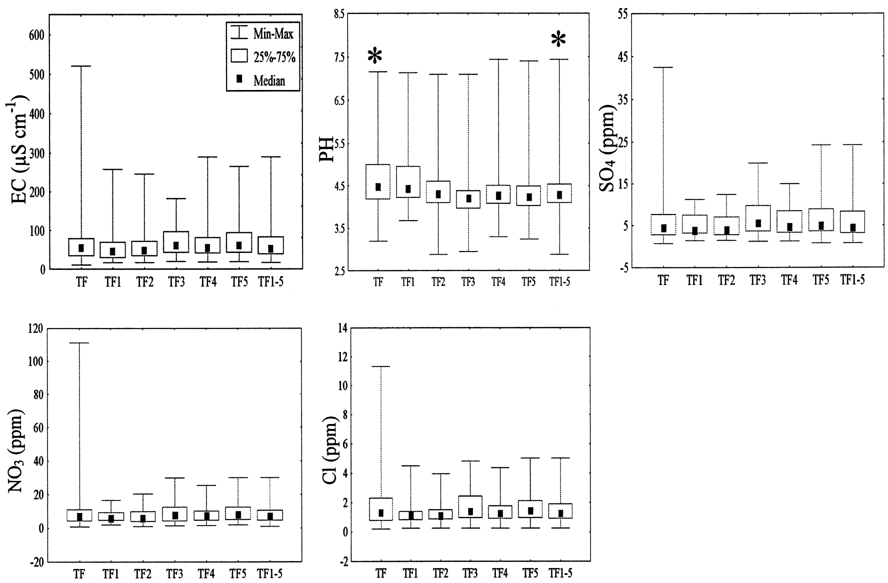

Figure 2. Heterogeneity of parameters in canopy throughfall. TF = daily measurement (n = 336). TF1 to TF5 = reference samplers of the monitoring program (n = 54). TF1-5 = observations of all five reference samplers included (n = 270). * = significant difference of TF and TF1-5.

ture the frequency distribution of the parent population. The latter seemed to be well captured with a two year measurement period.

To summarize, the overall heterogeneity captured with the setup of the reference sampling was equal or even higher (in case of soil solution). The latter was true even though number of observations were only 16, 5 and 7% of the high resolution time series for throughfall, soil solution and runoff measurements, respectively. Note that if all 5 samplers of the reference treatment were considered, number of reference observations compared to high resolution measurements were 80 and 23% for throughfall and soil solution, respectively. In addition to the spatial heterogeneity being higher, it is less time, work and cost consuming to measure spatial than temporal heterogeneity (e.g., collect five samples every 14th day instead of 1 sample every day). If the aim of a measurement program is to capture the heterogeneity of ion concentrations in throughfall and soil solution, the more efficient strategy seems to be the measurement of spatial rather than temporal heterogeneity. Regarding the measurement strategy for stream water a biweekly sampling seems to be well suited to capture the frequency distribution as long as time periods > 1 year are considered. If measurement programs capture the full heterogeneity of a sample, the long-term trends should also be determined correctly. However, if short term temporal patterns of time series and short term dynamics of processes are to be understood, high resolution measurements are a valuable tool as has been shown previously (Solo-Gabriele 1998; Laudon 1999; Larocque et al. 1998; Wilby et al. 1998; Jenkins et al. 1993).

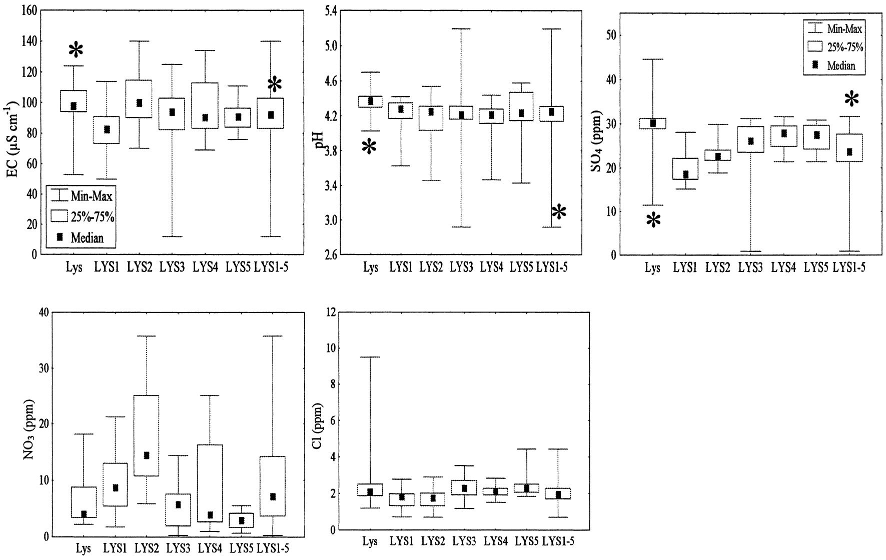

Figure 3. Heterogeneity of parameters in soil solution (90 cm depth). Lys = daily measurement (n = 437). Lys1 to Lys5 = reference samplers of the monitoring program (n = 22). Lys1-5 = observations of all five reference samplers included (n = 110). * = significant difference of Lys and LYS1-5.

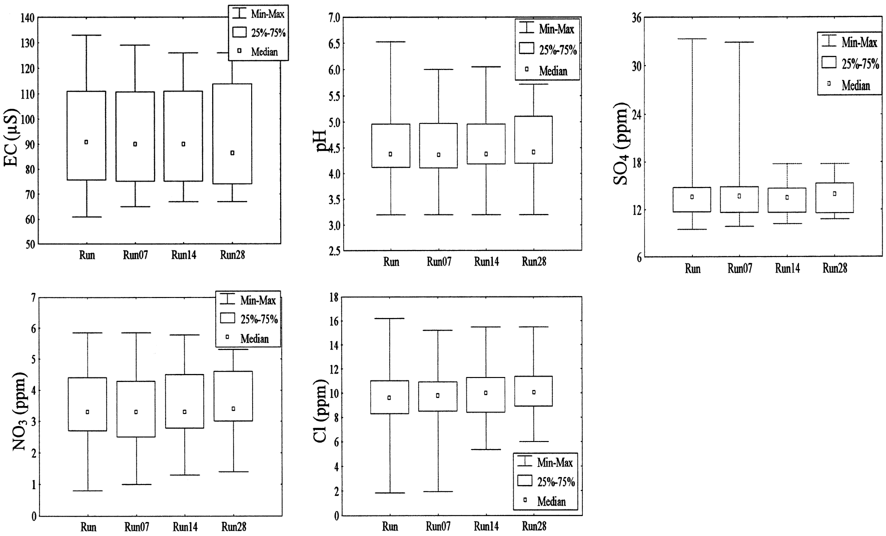

Figure 4. Heterogeneity of parameters in runoff. Run = daily measurement (n = 756). Run07, Run14, Run28 = reference sampling as weekly, biweekly and monthly measurement (n = 106, 53, 26). No significant difference between medians.

Error estimation of runoff fluxes

To estimate the error connected to the biweekly sampling of the reference time series, flux calculations of high resolution measurements were compared to the reference sampling. Results presented here refer to fluxes with runoff only. In principle, errors of ion fluxes with throughfall should not increase due to temporal integration, because bulk sampling should guarantee a quantitative measurement of ion fluxes at the sampling spot. Calculations of ion fluxes in soil solutions are generally problematic because of the high uncertainties involved in modeling water fluxes and setting them against concentration measurements of bulk samples. Thus, a comparison of high resolution measurements with the reference setup should include different model strategies which are beyond the scope of this paper.

Fluxes of Cl^-, NO_3^-, and SO_4^{2-} with runoff differed significantly between daily measurements and the biweekly sampling when short time periods (up to 6 or 7 months) were evaluated (for interpolation methods and calculation of % flux error see above; Figures 5, 6 and 7). Storm flow periods were the most crucial as solute concentration tended to change much more rapidly than under base flow conditions. Furthermore, associated ion fluxes were much higher due to higher water fluxes. As a consequence, the discharge peaks in the winter 1998/1999 were clearly reflected by the graphs of the cumulative ion flux errors.

However, the differences between measurement strategies as well as the difference between calculation methods became smaller over time. The SO_4^{2-}, Cl^-, and NO_3^- fluxes of both sampling strategies differed for the two year period in only 3, 10 and 5%, respectively (for each ion the interpolation method with the highest error was considered as worst case scenario; Figures 5, 6 and 7). Thus, results indicated for the calculation of ion fluxes with the runoff *Lehstenbach* that a biweekly sampling strategy with taking grab samples resulted in major errors when short time periods were evaluated. However, over longer time periods (> 1 year), errors became clearly smaller, because drawn samples represented more and more the overall heterogeneity of the parent population.

Regarding the differences between the interpolation methods, the autoregressive and the linear interpolation resulted in the smallest flux errors for all three elements over the whole time period considered. However, the difference between calculation methods was generally small. Only for Cl^- fluxes the stationary interpolation methods differed from the linear and the autoregressive interpolation by $\geqslant$ 10% even for the two year period. The relatively small difference between the interpolation methods was due to the high autocorrelation of the data (Table 1 and Figure 8). The calculated threshold of autocorrelation was very similar for the daily and the reference data set (Table 1). Obviously this statistical information was not lost by biweekly sampling. For all five parameters, the threshold values for autocorrelation were greater than 80 days (Table 1). Thus, the autocorrelation threshold exceeded the sampling interval by far. If data are autocorrelated for a time period longer than half the measurement interval, the error made with stationary or linear interpolation becomes clearly smaller than with time series which have a lower degree of autocorrelation or are totally random.

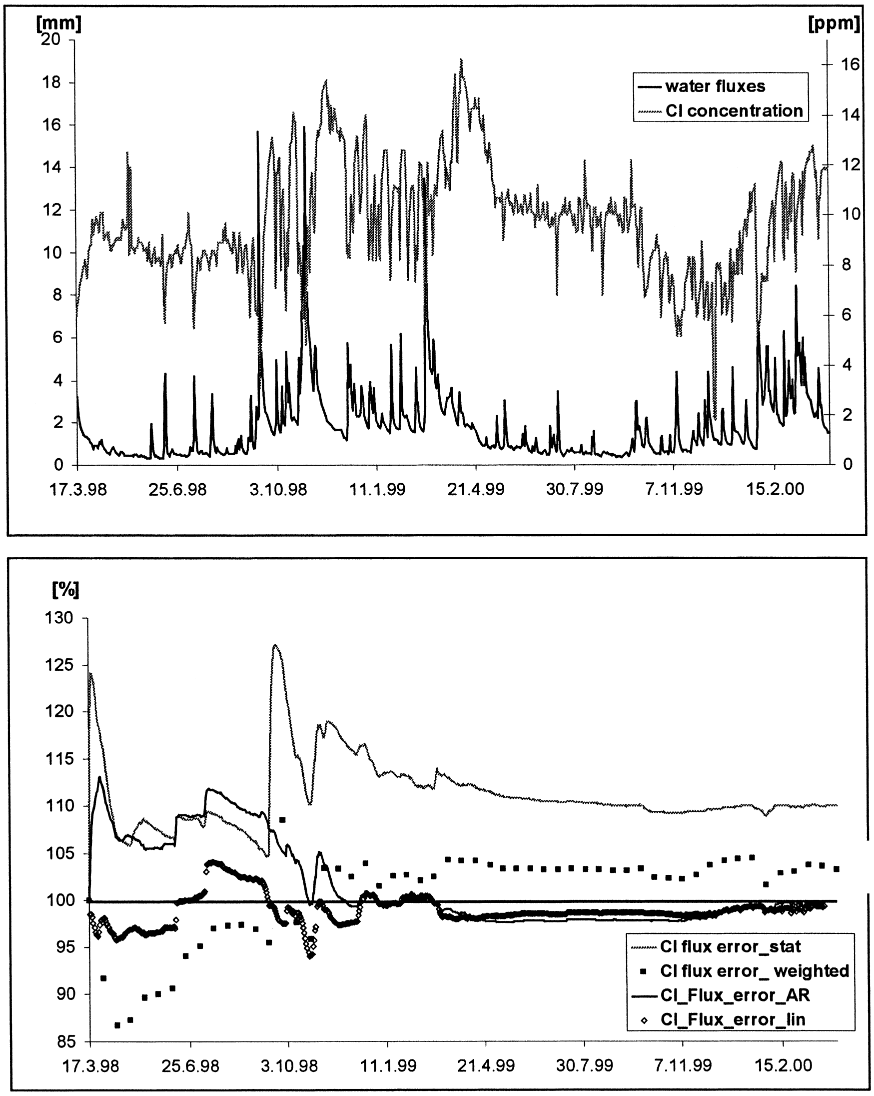

Figure 5. Daily Cl^- concentrations and water fluxes (upper panel) in the runoff *Lehstenbach*. Percentages of flux errors compared to daily measured fluxes are given in the lower panel for the stationary, the weighted, the AR- and the linear interpolation.

Theoretical considerations imply that dependent on the autocorrelation of concentration data different methods for flux calculations should be used. With a pronounced autocorrelation, the error included with interpolating between subsequent sampling days should be relatively small as long as the threshold value is clearly greater than the measurement interval. In contrast, if time series show little autocorrelation, it can be helpful to look out for a correlation to other parameters that

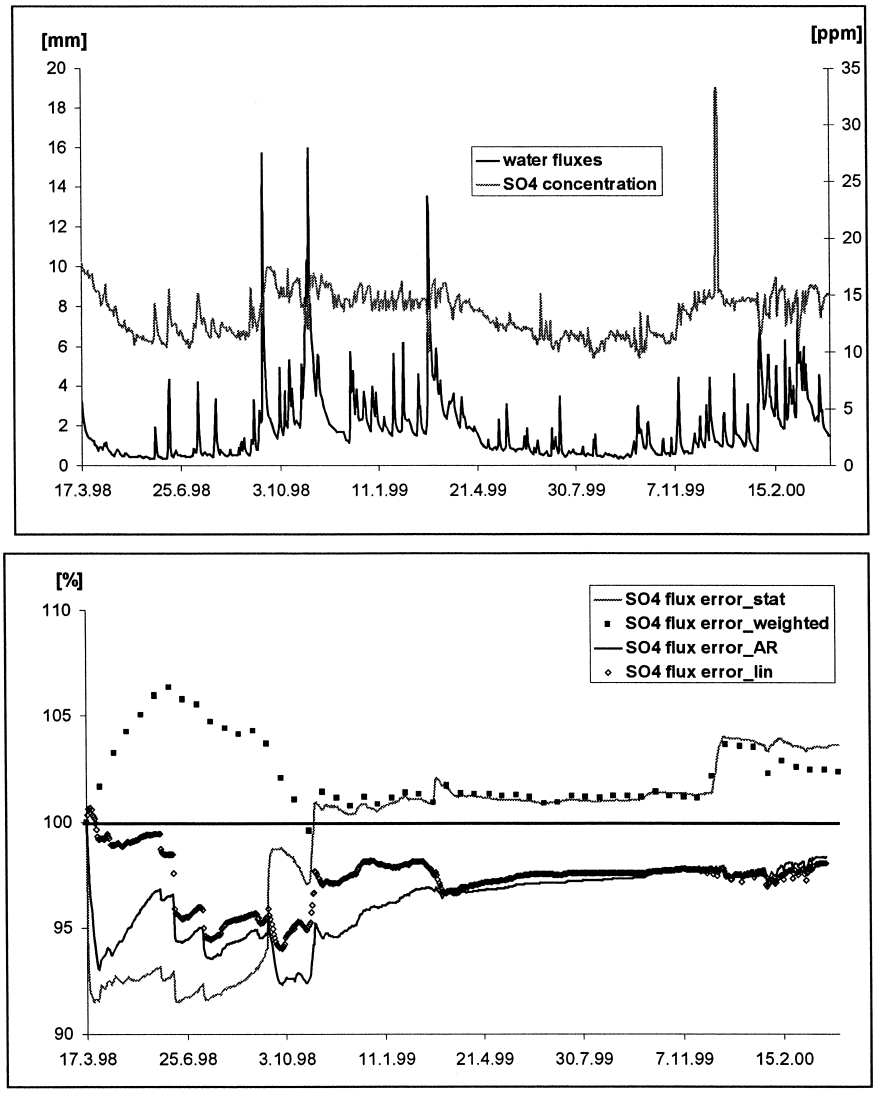

Figure 6. Daily SO_4 concentrations and water fluxes (upper panel) in the runoff *Lehstenbach*. Percentages of flux errors compared to daily measured fluxes are given in the lower panel for the stationary, the weighted, the AR- and the linear interpolation.

are measured at high temporal resolution, e.g., discharge or air temperature. If significant correlations are found, regression functions can be used to interpolate between subsequent sampling dates. At the *Lehstenbach* catchment, all of the investigated runoff fluxes (Cl^-, SO_4^{2-}, NO_3^-) showed a very weak correlation to either water flux or temperature. Furthermore, these functions might not be constant in

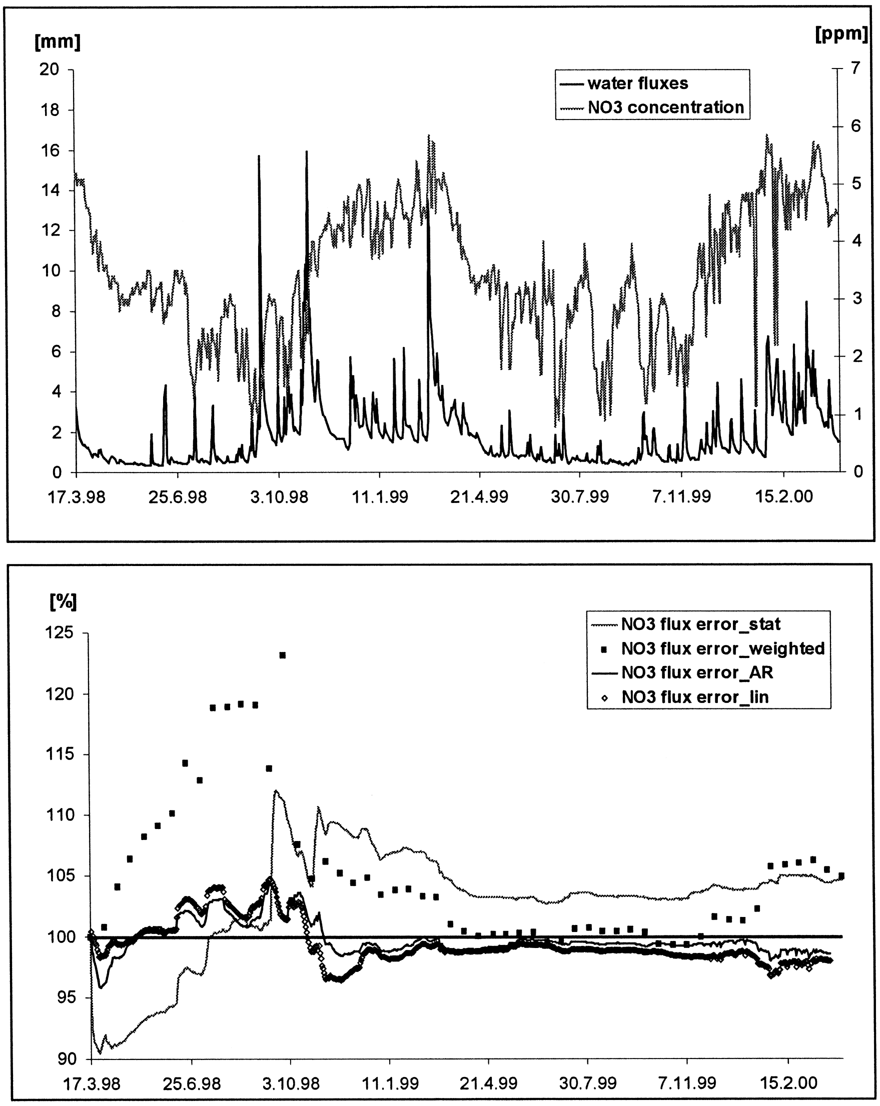

Figure 7. Daily NO_3 concentrations and water fluxes (upper panel) in the runoff *Lehstenbach*. Percentages of flux errors compared to daily measured fluxes are given in the lower panel for the stationary, the weighted, the AR- and the linear interpolation.

the long-term perspective (Bukaveckas et al. 1998), as has been shown to be the case for sulfate concentration in the *Lehstenbach* runoff (Lischeid 2001).

With time series that are random the weighted interpolation should be used, if time series > 1 year are available. If no high resolution measurements and thus no information about the shape of the autocorrelation function is available, we recommend to also use the weighted interpolation method. The latter is the only method

Table 1. Threshold values for autocorrelation of runoff data. RUN = high resolution measurement, RUN14 = reference sampling. EC = electrical conductivity.

Parameter	RUN lag (days)	RUN14 lag (days)
Cl^-	83	98
NO_3^-	90	84
SO_4^{2-}	81	98
PH	101	112
EC	104	98
Discharge	71	84

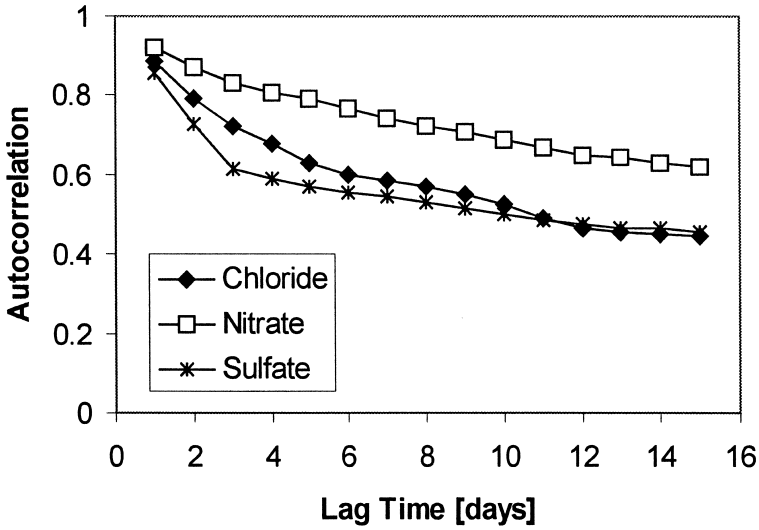

Figure 8. Autocorrelation of the daily solute concentration time series in the *Lehstenbach* runoff.

to avoid a systematic error caused by the unsuitability of the interpolation method with the shape of the autocorrelation function.

Conclusions

A general answer to the question if high resolution measurements are a gain of information or a waste of resources can obviously not be given for all systems and all types of questions asked. The monitoring program at the catchment *Lehstenbach* aims at assessing the maximum heterogeneity of ion concentrations, the determination of mass balances and the general assessment of critical ecosystem states. For the latter aims, our results indicate that a biweekly measurement strategy can be recommended. High resolution measurements with a daily measurement interval do not seem to be a suitable method (with respect to the additional benefit), because of the high efforts in cost, work and time resources and the comparably low information gain. To estimate maximum heterogeneity of ion concentrations (and thus temporal trends) it is less time and resource consuming to include spatial rather than temporal heterogeneity.

Errors of runoff fluxes due to temporal integration over 14 days will become relatively small compared to daily measurements if time periods > 1 year are considered. We recommend the weighted interpolation if time series show non autocorrelation or randomness. The linear interpolation should only be used if the threshold value of the autocorrelation function clearly exceeds the measurement interval. If no information about the autocorrelation function of the time series is available, the weighted interpolation method should be used. The weighted interpolation is also suitable with autocorrelated data but will most likely have a higher error compared to the autoregressive or the linear interpolation.

Generally, the introduced methods are applicable in all monitoring programs where ion concentrations and fluxes are measured. However, conclusions on temporal resolution of measurements do not apply to systems where ion concentrations in solutions have a low autocorrelation length. For example, urban and agriculturally used systems are very different in their dynamic (e.g., nitrate flushed through the system due to fertilizer or sewage application) as well as in the type of questions asked (e.g., leaching of harmful substances after pesticide treatment). Furthermore, temporal resolution of measurements in ecosystems of extreme hydrological conditions or temperatures (e.g., the subtropics or tropics) have to take into account that microbial turnover or hydrological extremes play a more dominant role. Our conclusions aim at the effects of temporal integration only and do not say anything regarding problems due to microbial turnover or gaseous losses from bulk samplers during long residence times in the fields.

We are aware that during times of restricted public monetary resources most researchers rather aim at switching from weekly to biweekly or monthly sampling interval instead of considering daily sampling. The aim of this study was to quantify the loss in information due to weekly or biweekly instead of daily sampling, which is crucial to know before switching to an even lower temporal resolution. Future research will be needed to quantify the loss in information due to monthly or bimonthly temporal integration of measurements.

Acknowledgements

This project was financially supported by the German Ministry of Education and Research, grant no. PT BEO 51-0339476. The Central Analytic of BITÖK was sampling and analyzing the reference data set. Runoff data were kindly provided by the Bavarian State Office of Water Management. We would like to thank Birgit Brunner for analytical help.

References

Bukaveckas P.A., Likens G.E. and Winter T.C. 1998. A comparison of methods for deriving solute flux rates using long-term data from streams in the Mirror Lake Watershed. Water Air Soil Pollut. 1: 277–293.

BML 1997. Dauerbeobachtungsflächen zur Umweltkontrolle im Wald Level II Methodenleitfaden. Bundesministerium für Ernährung, Landwirtschaft und Forsten, Bonn.

Butler T.J. and Likens G.E. 1998. Weekly and daily precipitation chemistry network comparisons in the eastern US: NADP/NTN vs MAP3S/AIRMoN. Atmos. Environ. 32: 3749–3765.

Dirks K.N., Hay J.E., Stow C.D. and Harris D. 1998. High-resolution studies of rainfall on Norfolk Island Part II: Interpolation of rainfall data. J. Hydrol. 208: 187–193.

de Vries W., Reinds G.J., van der Salm C., Draaijers G.P.J., Bleeker A., Erisman J.W. et al. 2001. Intensive monitoring of forest ecosystems in Europe, Technical Report 2001. EC-UN/ECE. Forest Intensive Monitoring Coordinating Institute, Brussels.

Draaijers G.P.J., Bleeker A., van der Veen D., Erisman J.W., Möls H., Fonteijn P. et al. 2001. Field inter-comparison of throughfall, stemflow and precipitation measurements performed within the framework of the Pan European Intensive Monitoring Program of EU/ICP forests. TNO report R 2001/140, UN/CEC-DG6. Netherlands Organisation for Applied Scientific Research, Apeldoorn.

Jenkins A., Ferrier R. and Waters D. 1993. Melt water chemistry and its impact on stream water quality. Hydrol. Process. 7: 193–203.

Kleemola S. and Forsius M. 1997. 6th Annual Report 1997. UN ECE ICP Integrated Monitoring. 6th Annual Report 116. The Finnish Environment Institute, Helsinki.

Larocque M., Mangin A., Razack M. and Banton O. 1998. Contribution of correlation and spectral analyses to the regional study of a large karst aquifer (Charente, France). J. Hydrol. 205: 217–231.

Laudon H. 1999. Spring Flood pH Decline in Northern Sweden: Towards an Operational Model Separating Natural Acidity from Anthropogenic Acidification. Licentiate Dissertation, Umea, Stencil no. 49.

Likens G.E. and Bormann F.H. 1995. Biogeochemistry of a Forested Ecosystem. Springer Verlag, New York.

Lischeid G. 2001. Investigating short-term dynamics and long-term trends of SO_4 in the runoff of a forested catchment using artificial neural networks. J. Hydrol. 243: 31–42.

Lischeid G., Alewell C., Bittersohl J., Göttlein A., Jungnickel C., Lange H. et al. 1998. Investigating soil and groundwater quality at different scales in a forested catchment: the Waldstein case study. Nutr. Cycl. Agroecosys. 50: 109–118.

Lischeid G., Kolb A. and Alewell C. 2002. Apparent translatory flow in groundwater recharge and runoff generation. J. Hydrol. 265: 195–211.

Manderscheid B. and Matzner E. 1995. Spatial and temporal variation of soil solution chemistry and ion fluxes through the soil in a mature Norway *spruce (Picea abies* (L.)Karst) stand. Biogeochemistry 30: 99–114.

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 Soil 176: 139–147.

Solo-Gabriele H.M. 1998. Generation of long-term record of contaminant transport. J. Environ. Eng. 124: 619–627.

Stoddard J.L., Jeffries D.S., Lükewille A., Clair T.A., Dillon P.J., Driscoll C.T. et al. 1999. Regional trends in aquatic recovery from acidification in North America and Europe. Nature 401: 575–578.

Stow C.D. and Dirks K.N. 1998. High-resolution studies of rainfall on Norfolk Island Part 1: The spatial variability of rainfall. J. Hydrol. 208: 163–186.

Ulrich B. 1989. Effects of acid precipitation on forest ecosystems in Europe. In: Adriano D.C. and Johnson A.H. (eds), Acid Precipitation: Biological and Ecological Effects (Advances in Environmental Science). Vol. 2. Springer Verlag, Berlin, pp. 189–272.

Wilby R.L., Wigley T.M.L., Conway D., Jones P.D., Hewitson B.C., Main J. et al. 1998. Statistical downscaling of general circulation model output: A comparison of methods. Water Resour. Res. 34: 2995–3008.