

**Difficulties in Deducing Temporal Changes in
Precipitation Chemistry from Snow and Ice Cores:
The Spatial Variability Problem**

Paper presented at the 8th Northern Res. Basins Symposium/Workshop
(Abisko, Sweden – March 1990)

R. C. Metcalf and D. V. Peck

Lockheed Eng. & Sciences Co., Las Vegas, NV-89119, U.S.A.

Depth profiles of chemical impurities found in snow and ice have usually been interpreted simply in terms of temporal changes in atmospheric concentrations of the species of interest. Measurements of pH and conductivity from individual snow stratigraphic layers sampled above 2,600 metres indicate local spatial variation in these parameters is sufficiently large to potentially mask temporal changes inferred from depth profiles. Inferences concerning past climatic variation based on assumed temporal chemical variations for a given depth profile are suspect, prior to adequate measurements of a given analyte's spatial variability in the immediate area of sampling. A method is presented for calculating the number of samples of a given stratigraphic layer necessary to achieve the required precision about the mean pH in a vertical ice profile.

Introduction

Chemical analyses of snow and ice have proven invaluable in: 1) assessing background acidity of precipitation in remote regions (Delmas and Gravenhorst 1983); 2) determining relative contributions of natural and anthropogenic emissions to the atmosphere (Wolff and Peel 1985); 3) observing the influence of fractional concentration on aquatic biota (Johanessen and Hendricksen 1978); and 4) observing preferential elution of solutes during spring melt periods (Davies *et al.* 1982). Depth profiles of chemical impurities found in snow and ice cores have usually been interpreted to be associated with temporal variation of atmospheric aerosols and solutes (Wolff and Peel 1985). Previous work implicitly assumed that

individual snow stratigraphic layers were uniform in chemical composition and concentration over a large area. This premise allowed solitary core or snow pit samples to be accepted as “representative” of a sampled site; any variation in chemistry with depth was attributed solely to temporal variation.

This study examines the spatial variability of snow layer electrochemistry to test the validity of implicit assumptions used to attribute changes in snowpack chemistry, with depth, only to variation with time. We investigate how representative a single sample is of a given layer’s electrochemical properties. The variability of pH and conductivity measurements is examined for a single fresh snow layer collected over a 6 m² area from an elevation of 3,230 m, and a melting layer collected over a 64 m² area from an elevation of 2,600 m. We also review the variability of new snow over several km² from Mt. Everest (collected from 5,500-7,000 m elevation), accounting for several sources of measurement error. After demonstrating a minimum spatial variation in fresh cold snow of ± 0.16 pH units ($2s$) in this study, the potential for spatial variation in pH masking temporal changes interpreted from core measurements is explored by applying our estimates of spatial variation and measurement error to three of the most rigorous snow core pH data sets. A method is presented for calculating the number of samples of a given stratigraphic layer necessary to achieve the required precision about the mean pH in a vertical profile.

Field Measurements of Snow Chemistry Spatial Variability

Colorado, USA

A single snowfall event was sampled from 10 to 31 h after deposition on March 9, 1987 in the Colorado Rockies at the University of Denver’s High Altitude Research Laboratory (elevation 3,230 m) on Mt. Evans (Hess *et al.* 1988; Rocchio *et al.* 1988). A total of 0.245 m² of snow was sampled in a random pattern within a 6 m² surface area. The 0.06 m thick snow layer was composed of broken and intact stellar crystals, with a density of 108 kg m⁻³. Samples were taken 1 to 2 mm beneath the surface (to avoid surface contamination) in a spruce forest clearing tens of metres across, using a Taylor-LaChapelle stainless steel snow density cutter (0.073×0.048×0.060 m). Air temperatures ranged from -25° C to -8° C. 56 snow melt samples were measured for conductivity, and 28 of these samples were measured for pH. In addition to the sample measurements, pH measurements were also conducted on field laboratory blanks and dilute sulfuric acid standards. Replicate measurements of pH were also collected for five samples. Sample pH was determined after a 3-minute equilibration period to allow a single operator to conduct the large number of determinations in a reasonable time period. Using this operational criterion, not all samples will be at equilibrium with the Orion Ross pH combination electrodes used for measurement, which introduces a possible mea-

surement bias (Metcalf 1987a). However, most modern studies use a similarly fixed “time to equilibrium”, rather than the more strict criterion of a change of less than 0.02 pH unit over two minutes, which can account for variations in electrode response times between samples (Metcalf 1987a; Davison and Harbinson 1988). Electrical conductivity was measured to a resolution of $0.1 \times 10^{-4} \text{ S m}^{-2}$ ($0.1 \mu\text{S cm}^{-1}$), using a PTI-10 meter with a Sproule dip cell (verified cell constant = 1.00).

Utah, USA

The last spring snowfall event was sampled 14 days after deposition (April 3, 1987) at Duck Creek, Utah near Navajo Lake (elevation 2,600 m) (Metcalf *et al.* 1988). A total of 0.043 m^2 of melted and refrozen snow was sampled in an “X” pattern within a 64 m^2 surface area. The sampled layer was in an aspen forest clearing with no trees within tens of metres of the sampling site. The 0.05 m thick snow layer was composed of destructively (equitemperature) metamorphosed grains (LaChapelle 1969), rounded to subrounded in character. Sampling was done by removing 0.01 m of surface grains and scraping up the remaining snow from the layer with pre-washed (and rinsed) 0.25 dm^3 polyethylene beakers used to measure the melted samples. Air temperature ranged between -10° C and $+10^\circ \text{ C}$. 17 samples were melted and measured within 4 hours for pH and conductivity (as described in the previous section) at a field laboratory located at Duck Creek. Operational equilibrium pH values were defined after three minutes of measurement (as for the Colorado samples).

Mt. Everest, Tibet

Jenkins *et al.* (1987) presented the results of pH measurements from individual storm snow deposits collected during a mountaineering expedition on the north face of Mt. Everest on April 1, 5, 12, and May 6, 1986. Samples were collected in precleaned 0.125 dm^3 containers from the uppermost 0.05 m of snow immediately following a storm (Jenkins *et al.* 1987). Multiple samples were taken at a given elevation in even-deposition zones from a $3 \times 3 \text{ m}$ random matrix grid. Up to 0.060 dm^3 was allowed to melt at 5,600 m elevation on Mt. Everest. These samples were measured for pH and conductivity in the United States within 2 to 6 weeks of melting. An Orion Ross pH combination electrode was used to determine pH (as for the Utah and Colorado samples).

Discussion of Observed Variability of Snow Chemistry

Fig. 1 shows a histogram of conductivity for the 56 Colorado snow samples, measured at 13° C . No temperature corrections were applied to these data to avoid introducing additional sources of error. Atmospheric CO_2 concentrations contribute about $0.6 \times 10^{-4} \text{ S m}^{-1}$ ($0.6 \mu\text{S cm}^{-1}$) at 13° C to these samples. Effects of CO_2

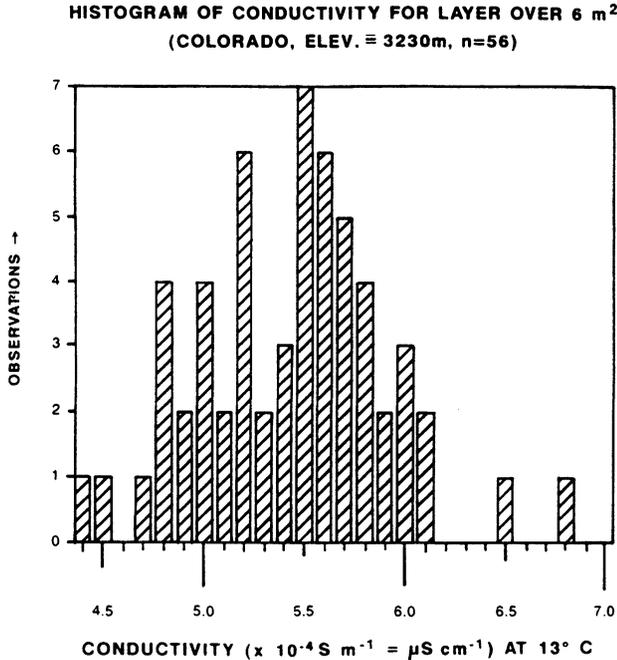


Fig. 1. Histogram of snow melt conductivity at 13° C for 56 samples of one storm deposit over 6 m², within hours of deposition at 3,230 m in Colorado, U.S.A.

on conductivity were constant in deionized water blanks measured along with the snow samples. For such low conductivity meltwaters (from a common chemical source), the conductivity is a linear function of major ion concentrations (Rossum 1975). Because the observed conductivity varies from 4.4 to $6.8 \times 10^{-4} \text{ S m}^{-1}$ at 13° C, the major ion concentrations in this snow layer probably vary by about the same amount, ± 50 per cent. The observed mean and median conductivity values are $5.5 \pm 0.9 (2s) \times 10^{-4} \text{ S m}^{-1}$ at 13° C. Conductivity measurements to within $\pm 0.2 \times 10^{-4} \text{ S m}^{-1}$ at a constant temperature are fairly easy to obtain rapidly, enabling large numbers of samples to be analyzed to a high precision. The importance to this study is that significant differences in cold snow layers' melt conductivity (and hence chemistry) are easily measured within a few hours of deposition, without the additional sources of error present in the snow pH measurements discussed below.

Fig. 2 presents a bivariate plot of the observed electrical conductivity and pH data for the Colorado snow samples. The ellipse is an estimation of the long-term (among-batch) measurement error, given as $\pm 2s$ about the median value (represented by a triangle in Fig. 2). If the snow layer actually is a constant pH and conductivity over the 6 m² area sampled, only 1 out of every 20 measurements should plot outside of the ellipse. 19 of the 28 data points fall outside of the ellipse, indicating that spatial variability is not negligible when interpreting temporal varia-

Spatial Variability in Snow Chemistry

pH AND CONDUCTIVITY OF NEW SNOW LAYER OVER 6 m² (COLORADO, ELEV. = 3230 m, n=28)

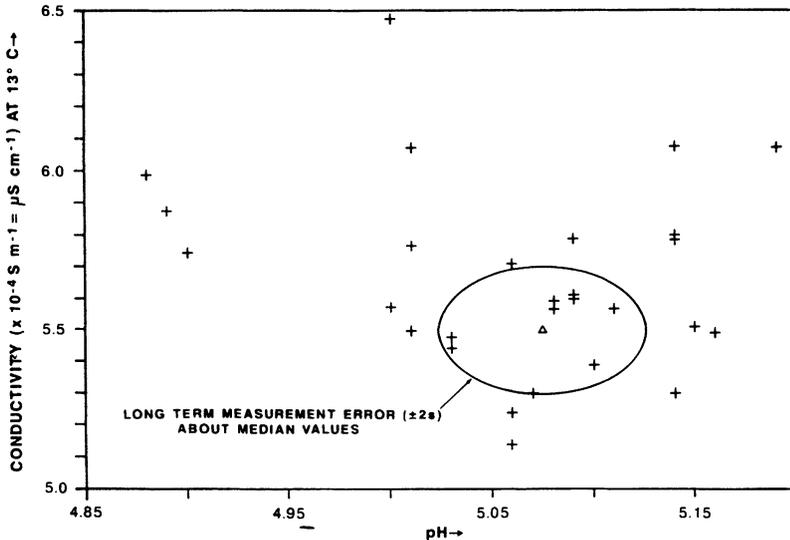


Fig. 2. Bivariate plot of pH and conductivity of Colorado snow melt showing natural spatial variability over 6 m² (crosses plotting outside the ellipse), an estimate of sample values within the long-term measurement error (crosses plotting within the ellipse), and the median values observed for the layer (triangle centered in the ellipse).

bility from cores in this snowpack. Table 1 shows that the range of observed pH values for this distribution is 0.31 units and $2s = \pm 0.16$ pH units. To a good approximation, any depth variation of pH in this snowpack would have to be greater than ± 0.16 (or 0.32) pH units in order to be detected above the background of observed spatial variability in pH.

Fig. 3 shows the observed pH and electrical conductivity data for the partially melted and refrozen Utah snow layer. Again, the ellipse is an approximation of the long-term measurement error about the layer's median value (represented by a triangle). Only one of 17 values plot within the ellipse shown in Fig. 3. 94 per cent (16 of 17) of the measurements show variation which would normally be attributed to spatial variation, rather than to measurement error. The range of pH observed for the Utah snow layer (1.95 pH units, Table 1) and $2s$ value (1.18 pH units) is about an order of magnitude greater than for the Colorado snow samples. Increasing chemical variability within a snow layer is to be expected whenever solutes are redistributed by melting and refreezing.

The Utah snow samples also demonstrate the great difficulty in obtaining accurate pH measurements in waters approaching the pH and conductivity of reagent

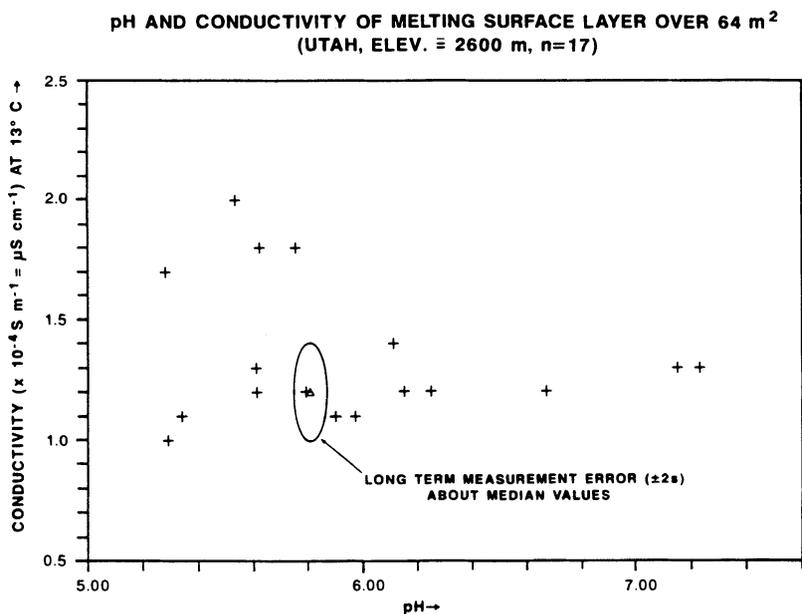


Fig. 3. Bivariate plot of pH and conductivity of Utah snow melt showing natural spatial variability over 64 m² (crosses plotting outside the ellipse), an estimate of sample values within the long-term measurement error (crosses plotting within the ellipse), and the median values observed for the layer (triangle centered in the ellipse).

water used to prepare analytical reagents and blanks. The 1×10^{-4} M HCl quality control check standard measured 4.56 pH units at the end of the analytical run, rather than the expected 4.01 (not including the liquid junction potential error). This 0.55 pH unit error in a dilute acid standard indicates large voltage errors associated with junction clogging (Metcalf 1984a), crystal precipitation within the junction (Metcalf 1984b), or buffer solution carryover (Metcalf 1987b) within the junction's ceramic frit. Consequently, 0.55 pH units were subtracted from each measurement value. The first three pH measurements following buffer calibration gave the only values above pH 6.6, and may indicate a larger pH measurement error than usual (± 0.05 to 0.07 pH units (2σ), Metcalf 1987a; Metcalf *et al.* 1989) due to buffer carryover or junction clogging. It should be stressed that such errors are a normal part of snow melt pH measurements in such dilute solutions. They probably occur in many other studies, but are not detected without a strict quality control program of measurements in known dilute standards (Metcalf 1987a, 1987b; Metcalf *et al.* 1988).

Little variation was observed in the 2σ values of pH recorded for the Utah samples recorded after 3 minutes (1.18 pH units) or the measurements at one-minute intervals when extrapolated (with a linear regression of pH, log time (min)) to 15 minutes (1.21 pH units) or 4 hours (1.19 pH units). Although there may be a

Spatial Variability in Snow Chemistry

Table 1 - Observed Variability During pH Measurements of Alpine Snow Layers

| | Location: Colorado ¹ | Utah ¹ | Mt. Everest ² | | | |
|--------------------------|---------------------------------|-------------------|--------------------------|-------------|-------------|-------------|
| | | | Storm 1 | Storm 2 | Storm 3 | Storm 4 |
| Elevation (m): | 3,230 | 2,600 | 5,500-5,800 | 5,500-5,800 | 5,900-6,300 | 5,500-7,000 |
| Reference ³ : | 1,2 | 1,3 | 4,5 | 4,5 | 4,5 | 4,5 |
| Snow Condition: | Fresh | Some Melt | Fresh | Fresh | Fresh | Fresh |
| Maximum: | 5.19 | 7.23 | 6.90 | 6.50 | 5.70 | 6.90 |
| Minimum: | 4.88 | 5.28 | 5.82 | 5.54 | 5.27 | 6.40 |
| Range: | 0.31 | 1.95 | 1.08 | 0.96 | 0.43 | 0.50 |
| Mean: | 5.06 | 5.96 | 6.56 | 6.14 | 5.52 | 6.64 |
| 2s: | ±0.16 | ±1.18 | ±0.56 | ±0.55 | ±0.25 | ±0.29 |
| n: | 28 | 17 | 21 | 22 | 15 | 18 |
| Percentiles | | | | | | |
| 2.5th: | 4.88 | 5.28 | 5.82 | 5.54 | 5.27 | 6.40 |
| 5th: | 4.89 | 5.28 | 6.09 | 5.58 | 5.27 | 6.40 |
| 25th: | 5.01 | 5.61 | 6.48 | 6.03 | 5.41 | 6.50 |
| 50th: | 5.08 | 5.81 | 6.65 | 6.19 | 5.57 | 6.63 |
| 75th: | 5.13 | 6.15 | 6.77 | 6.31 | 5.63 | 6.78 |
| 95th: | 5.16 | 7.23 | 6.89 | 6.48 | 5.70 | 6.90 |
| 97.5th: | 5.19 | 7.23 | 6.90 | 6.50 | 5.70 | 6.90 |

¹ Measurements performed within 4 h of melt at a field laboratory.

² Measurements performed in USA weeks after sampling.

³ References: (1) Original measurements from this study; (2) Hess *et al.* (1988); (3) Metcalf *et al.* (1988); (4) Jenkins *et al.* (1987); (5) Unpublished data from J. I. Drever.

measurement bias for these samples, our main point is that there is a substantial spatial variation in pH for one snow layer within 64 m².

The results from the Mt. Everest snow samples recorded in Table 1 obviously include the confounding errors possible from dust in the snow chemically interacting during the several week long transport process from Asia (Metcalf 1984c; 1987b). Despite the possibility of higher pH values caused by melt interactions with natural rock dust, the 2s values of the four Mt. Everest storm deposits are ±0.25, ±0.29, ±0.55, and ±0.56 pH units (Table 1). These values are in between the 2s values of the Colorado (±0.16 pH units) and Utah (±1.18 pH units) snow layers, that we have measured using the same type of electrode.

Since the Colorado and Utah samples may include chemical input from the surrounding forests, they may exhibit more spatial variability than snow and ice cores from remote glaciers above the tree line. The possible chemical interactions of the Mt. Everest snow samples during shipping may also have increased the “apparent” spatial variability for a given storm layer.

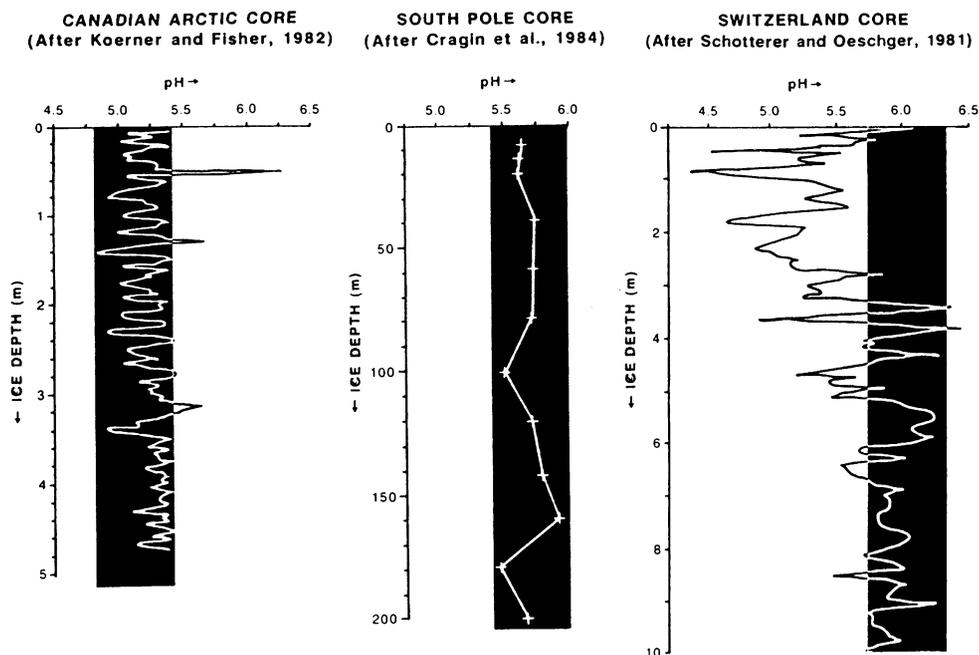


Fig. 4. The minimum spatial variability for a fresh snow layer (0.32 pH units) observed in this study (black area), arbitrarily superimposed on three of the most rigorously-measured pH profiles (after Koerner and Fisher 1982; Cragin *et al.* 1984; Schotterer and Oeschger 1981; Oeschger *et al.*, 1977) from snow and ice cores demonstrates the potential “noise” from spatial variability which could mask temporal variations during climatic reconstructions. All cores shown have the same relative pH scaling (x axes), but different depth scaling (y axes) in order to highlight differences in the shorter cores. The spatial variability mask is arbitrarily placed on the profiles because the median pH values could not be calculated without the raw pH data in several cases, but this has no effect on the qualitative conclusion that spatial chemical variability is an important source of “noise” in such studies.

Some of our critics have suggested that the variability we have observed is caused by sampling ice volumes that are too small, and represents fine scale features that are “smoothed out” by larger samples taken in ice core research. The sample volumes that we have used in this study are over 0.200 dm^3 , while most ice core samples are between $0.001\text{-}0.010 \text{ dm}^3$. During careful CO_2 gas analyses in Antarctic ice cores, Neftel *et al.* (1985) have observed no variation of CO_2 concentration in ice samples ranging from 0.001 to 1.000 dm^3 , which is the upper limit of sample volume in most core studies.

Assuming the lowest observed $2s$ value for this study (± 0.16 pH units) is representative of typical snow spatial variability, should this effect be considered in

any climatic reconstructions from snow chemical profiles with depth? At present, there is insufficient information available (specifically, information on chemical spatial variability with depth at the core site) to answer this question quantitatively.

An attempt to qualitatively demonstrate the potential magnitude of the spatial variability problem for temporal interpretations from snow and ice cores is given in Fig. 4. These pH profiles with depth represent some of the most precise and accurate work yet published (Fig. 4; Koerner and Fisher 1982; Cragin *et al.* 1984; Schotterer and Oeschger 1981; Oeschger *et al.* 1977). If a ± 0.16 pH unit spatial variability is superimposed on these profiles arbitrarily (without having all the raw pH data to calculate the median value for each core), any trends apparent in the Arctic and Antarctic cores are effectively masked and disappear. This qualitative result indicates that spatial variability of snow layer chemistry is a critical source of "noise" that must be considered in any climatic reconstruction from ice cores.

Additionally, the Swiss ice core from the very cold Colle Gnifetti accumulation area of Gornergletscher (10 m temperature = -14° C) showed possibly greater pH variability from melt (Schotterer and Oeschger 1981), which occasionally is observed at the coring site (Oeschger *et al.* 1977). For such cases when cores contain evidence of melt, the spatial variability of the Utah snow layer (± 1.18 pH units) may be more appropriate than the smaller Colorado snow variability arbitrarily superimposed over Fig. 4. This would mask even more trends than the presentation in Fig. 4.

Comparison with Previous Studies

Kumai (1985) has observed a substantial variation with distance from a coal-fired power plant in Fairbanks, Alaska, for the pH of 0.05 m thick snow samples ($n = 36$) measured in April, 1973. pH values decreased from 7.50 near the power plant to 5.60 at a site 20 km downwind. Conductivity of the snow melt ranged from 45×10^{-4} S m^{-1} at 25° C near the plant to 3.99×10^{-4} S m^{-1} (μ S cm^{-1}) at 25° C for snow at the site 20 km away. Kumai (1985) contended that the "acid" snow (near 5.6 pH unit background values) was chemically altered to alkaline snow by alkaline flyash from the power plant.

Brimblecombe *et al.* (1985) noticed a highly variable chemical composition along a 700 m transect through a small, Scottish catchment in winter 1984. 15 snow pit samples gave what they termed "coefficients of variance" of greater than 50 per cent for most of the major ions while pH varied by ± 0.10 pH units ($\pm 2s$; equivalent to about ± 130 μ E dm^{-3}) about the mean pH of 3.56. Brimblecombe *et al.* (1985) found that "the variability of both fresh and aged snows is so large that it is difficult to show any statistically significant compositional differences between them."

Schemenauer *et al.* (1985) analyzed the spatial chemical variations of an Ontario, Canada snowpack (compositing individual snow layers) by taking 5 cores at

each site and analyzing 3 cores taken several metres apart. Typical coefficients of variation for individual analytes were less than 10 per cent, except where concentrations were "very low". On one day, snow cores from five different sites tens of km apart (over an area of 22,500 km²) had coefficients of variation "normally 24 per cent or less for the major ions and pH" (Schemenauer *et al.* 1985). These comparisons would be more meaningful if distributions, or additional descriptive statistics, were given for each chemical parameter.

Jones (1985) has noted the change of H⁺ concentration associated with melt water formation and redistribution in the snowpack of a boreal forest near Lac LaFlamme, Quebec, Canada. Although Jones was able to map stratigraphically the "mesostructure" of the pack using relative H⁺ concentration differences between layers, in individual snow strata, he observed changes in H⁺ concentration of up to 50 per cent over the 4 m horizontal distance between his sites A and B. Apparently, the greater the amount of liquid water present in the pack, the resulting distribution of solutes within the snow is more complex.

Laird *et al.* (1986) noted differences in pH of from 0.01 to 0.20 pH units between six samples of surface snow and adjacent snow core samples taken in the Cascades and Sierra Nevada, but since the snow cores were not segmented, it was not possible to ascertain if the observed pH differences were significant, according to Laird *et al.* (1986). In fact, these differences are not significant when compared to the duplicate precision (± 0.11 pH units) estimated with one standard deviation by Laird *et al.* (1986). Changes of up to 118 per cent in calcium and 150 per cent in measured sulfate concentrations inside and outside 4 m² wooden boxes in the pack were presented, but sample losses from meltwater removal were believed to be insignificant for the purposes of the study.

Holdsworth and Peake (1985) observed changes with depth of up to 0.4 pH unit for snow melt pH values near 5.3 pH units from 5,340 m on Mount Logan in the Yukon Territory of Canada. Some measurement difficulties were noted, and the pH measurements were used mainly for reconnaissance of "the larger acid events so that the expensive and time-consuming nitrate, sulfate, and chloride determinations could be carried out at strategic points," according to Holdsworth and Peake (1985).

To summarize, in the few cases in which the spatial variability of individual snow layers has been carefully measured, it has shown the potential to mask much of the temporal variation in snow core climatic reconstructions. What can be done to minimize or eliminate the effect of the spatial variability within snow layers on inferred temporal changes during core analyses? Obviously analyses of two separate cores are important, but costly. At least a cursory examination of the snow chemistry spatial variability of surface layers should be a requirement for drill site selection. However, much more research is required to evaluate how many past inferences of temporal changes in the snow chemistry of cores really are valid.

Additional work is necessary to refine the measurement precision and accuracy

of pH measurements in such low ionic strength solutions. Numerous errors have been quantified for the Orion Ross pH combination electrodes used in our study including: the residual liquid junction potential contribution (+0.055 pH units; Metcalf 1987a), the stirring error contribution (−0.35 pH units; Metcalf *et al.* 1990), the error from KCl spiking (0.02 to 0.09 pH units from 0.01M to 0.19M KCl; Metcalf *et al.* 1990) and larger, varying errors from CO₂ gas transfer (Metcalf 1984c; Cragin *et al.* 1984; Koerner and Fisher 1982), ionic interaction with sediment in the sample (Metcalf 1984c), non-classical reference junction errors (Metcalf *et al.* 1989), or the failure to implement measurements of dilute acid pH standards to assure measurement quality (Metcalf 1987a; 1987b).

Another approach has been to acidify snow melt to 4.65 pH units and perform a very accurate acid neutralizing capacity (ANC) titration to within ±0.2 μE dm^{−3} (Legrand *et al.* 1982). Obviously, there is pH measurement uncertainty in adding known amounts of acid to reach the 4.65 pH unit starting point of these titrations. In their original work using ANC titrations to measure snow core acidity rather than pH measurements, Delmas and Aristarain (1978) measured acidities ranging from about −15 to +15 μE dm^{−3}. Most samples ranged from −2 to +4 μE dm^{−3} ANC (negative ANC values represent acidity) with an experimental error of ±1 μE dm^{−3}, according to Delmas and Aristarain (1978). It is easy to see that the experimental error is about 30 per cent of the measured signal in this case, and it is possible that careful pH measurements might give more precise results.

Legrand and Delmas (1985) have measured the H⁺ acidity variations for recently deposited snow along a 430 km transect in East Antarctica, finding variations of 0.60 to 2.57 μE dm^{−3} H⁺ (equivalent to 6.22 to 5.59 pH units, respectively), with a precision of ±0.2 μE dm^{−3} H⁺ (Legrand *et al.* 1982). Table 2 shows that a ±0.05 pH unit precision gives more precise results than the titration method of Legrand *et al.* (1982) at a pH of 6.00 and above. At the higher observed H⁺ concentrations (2.57 μE dm^{−3} = 5.59 pH units), a pH measurement error of ±0.05 pH units yields a precision of ±0.28 μE dm^{−3}, as compared to the ±0.2 μE dm^{−3} precision of the titration method. Clearly, this is an area where additional work is necessary to determine the most suitable method for measuring acidity in a given study.

Table 2 = Measurement Error of pH in terms of concentration at a given pH¹ (Measurement error ≡ ±0.05 pH units.)

| pH of interest | ±0.05 pH error (μE dm ³) |
|----------------|--------------------------------------|
| 3.00 | ±109 |
| 4.00 | ±10.9 |
| 5.00 | ±1.09 |
| 6.00 | ±0.11 |
| 7.00 | ±0.01 |
| 8.00 | ±0.001 |

¹ Concentration calculations assume activity coefficients of 1.00.

Measurements Necessary to Minimize Effects of Spatial Chemical Variability on Temporal Interpretations of Ice Cores

The prior sections document the poorer precision (much greater than the laboratory measurement precision) from spatial variation of pH and conductivity measurements of snow within a given stratigraphic horizon. How does one quantify the number of samples n in a given stratigraphic layer which must be measured in order to minimize the effects of spatial chemical variability on the precision about the mean value for a constant number of layers (a vertical profile)? One approach that shows promise is the use of spatial autocorrelation techniques (Jumars 1978; Bivand 1980; Cliff and Ord 1981; Thrush *et al.* 1989), although some aspects are yet to be resolved for the analysis of vertical chemical profiles. This approach is beyond the scope of this paper.

Based on the equation for the standard error about the mean (Freund 1971), one can derive an estimate for the number of measurements necessary to sample a layer in an ice core for a given precision about the pooled mean value from the layers under consideration

$$n = \left(\frac{\hat{s}_p}{\hat{s}_{m(n)}} \right)^2 \quad (1)$$

We have performed a Monte Carlo simulation assuming a profile of 20 “identical” stratigraphic layers (having the same mean pH value of 5.65) with an approximately normal distribution of pH within a layer. Ideally, such a measured profile should yield a vertical line of pH 5.65 through the 20 depth points representing mean pH values for each layer (Fig. 5). In practice, n points per layer measured for each profile of twenty layers were chosen from a random number table in Zar (1984), with an approximate 95 per cent confidence interval (± 0.31 pH units) in the range we have observed (Table 1). If the computed pH value for one of the 20 layers fell outside 5.65 ± 0.31 pH units, it was accepted for the profile, but never more than once per 20 layers. \hat{s}_p is the standard deviation about the mean value of the n samples used to approximate the spatial variability in a layer. $\hat{s}_{m(n)}$ is the standard deviation about the grand mean for 20 layers of n samples $\hat{s}_{m(n=3)}$ represents $20 \times 3 = 60$ samples).

In practice, our Monte Carlo simulation yielded an \hat{s}_p value of 0.20 pH units for $n = 1$ (Fig. 5), which is a likely value to be measured in the field. The mean profiles presented in Fig. 5 converge (at ever decreasing rates) toward a vertical line of pH 5.65 with increasing number of samples in each layer. Substituting $0.20 = \hat{s}_p$ and the pH measurement precision, $0.025 = \hat{s}_{m(n)}$ yields an estimate of 64 samples needed to lower the “noise” from spatial variability within a layer to the level of the pH measurement precision (Fig. 6). For an ideally sampled profile, \hat{s}_p is assumed to be 0.16 pH units (0.5×0.31) which results in 39 samples necessary to make the precision of the grand mean pH equal to the pH measurement precision. After 20

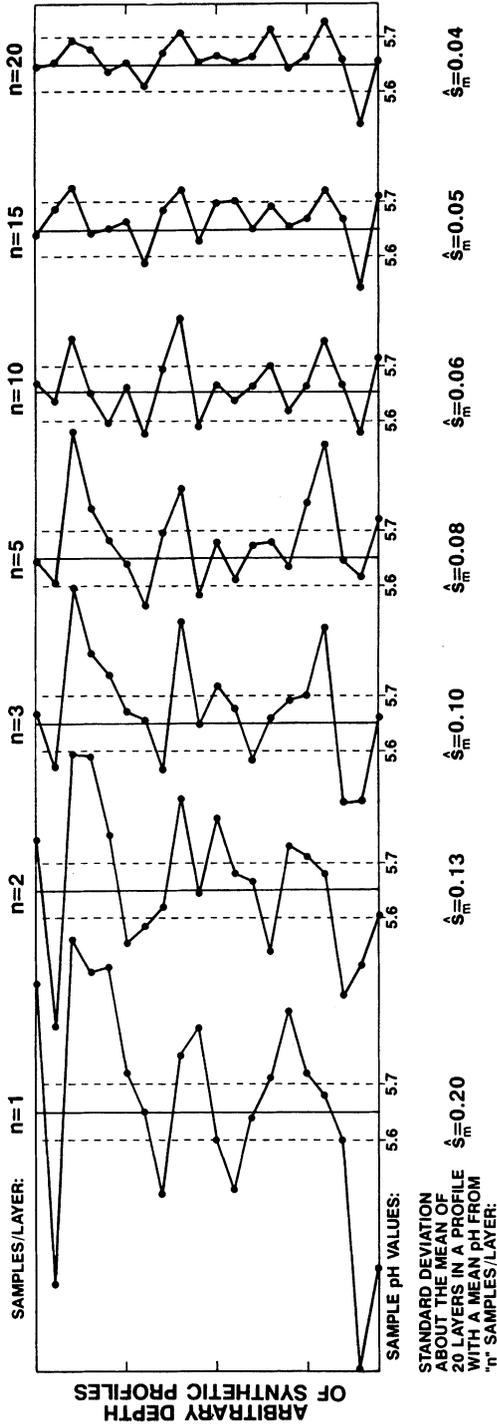


Fig. 5. Monte Carlo simulation of seven different vertical profiles of 20 "identical" ice layers with a mean pH of 5.65. Ideally, each profile should be plotted as the vertical line at pH = 5.65. Two times the pH measurements precision ($s \equiv 0.025$) is plotted as dashed lines on either side of the ideal mean value. Each profile is sampled from a random number table as detailed in the text, and only mean values only for the 20 stratigraphic layers are presented. After 20 samples are taken for each layer, the precision about the grand mean ($s_m(n=20) \equiv 0.04$) is still larger than the pH measurement precision, which is due to pH spatial variability within layers.

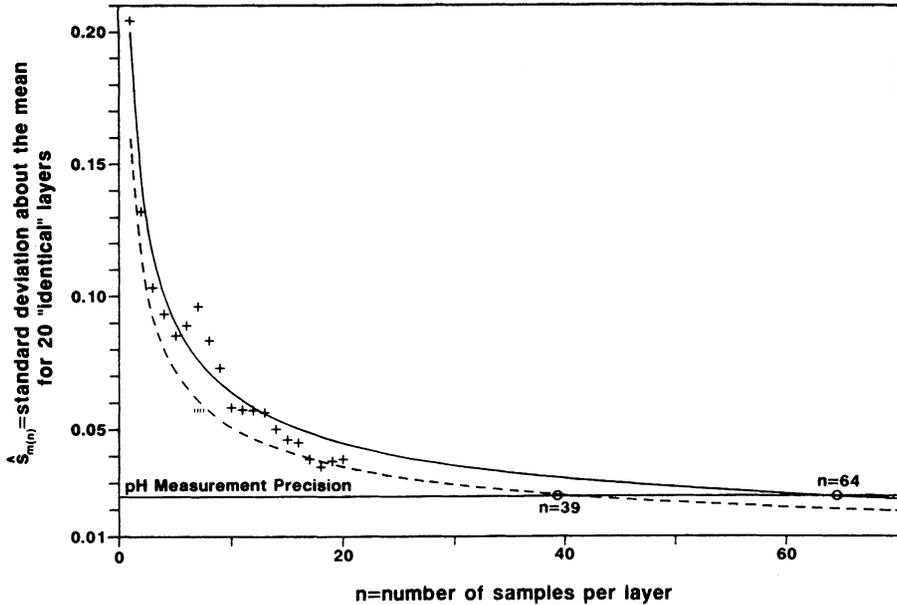


Fig. 6. Standard deviation about the mean for 20 mean pH values (the grand mean) from "identical" layers as a function of ice samples measured per stratigraphic layer.

samples per layer, our Monte Carlo simulation is approaching the dashed curve which equals the pH measurement precision after 39 samples (Fig. 6).

Obviously, the practice of quoting measurement precision for the precision about the mean of n samples taken from an ice core is inappropriate for temporal interpretations. Also, the common practice of obtaining only one or two uncontaminated ice samples per core layer (although understandable from logistics and costs) makes quantitative deductions about past climates very difficult. Finally, a direct consequence of Eq. (1) is that without an estimate of the spatial variability within a stratigraphic layer, there can be no estimate of the number of samples needed to achieve a required precision for the profile's grand mean.

Most studies do not adequately account for spatial variability of analytes during interpretations of past climates from ice cores. One outstanding exception is the work of Neftel *et al.* (1985), who analyzed more than twenty samples per annual layer (for five stratigraphic layers) in an important study relating the CO_2 values in ice cores to the values in past atmospheric air. For Neftel *et al.* (1985), Eq. (1) reduces to $(10 \text{ ppm CO}_2 / 2.8 \text{ ppm CO}_2)^2 = n = 13$ samples needed to lower the effects of CO_2 spatial variability to the measurement precision. Although costly, and logistically difficult, the careful sampling demonstrated by Neftel *et al.* (1985) is required in order to enable insightful climatic interpretations from chemical measurements of ice cores.

Conclusions

The electrical conductivity and pH of individual snow layers show a rather large spatial variability in fresh or aged alpine snows. Redistribution of solutes during melt and refreezing increases the observed electrochemical variability for a given layer. Studies which attempt to infer the temporal variation of snow chemistry from depth profiles must show that the spatial variability of a given layer is insufficient to mask any perceived changes with depth (time) between layers. Although pH and conductivity data are presented in this study, the general principles should hold for any chemical parameter measured in a snow pit or ice core. Inferences concerning past climatic variation based on assumed temporal chemical variations for a given depth profile are suspect, prior to adequate measurements of the chemical parameter's spatial variability in the immediate area of sampling. Additional research is necessary to optimize the methods of quantifying spatial chemical variation, and the required sample numbers per stratigraphic layer, in climatic reconstruction studies using snow and ice chemical profiles with depth.

Acknowledgements

J. Rocchio, R. Reiner, and L. Reiner assisted at the Colorado site. M. Stapanian, R. Hoenicke, J. Baker, W. Kinney, and C. Moyer assisted at the Utah site. J. Drever kindly sent us the unpublished Mt. Everest pH data, as measured by M. Spencer, for detailed statistical analyses. R. Gerlach, S. Thrush, M. Stapanian, and J. Hewitt provided statistical insights. D. Heggem, G. Pearson, and J. Baker were instrumental in their support of this project at the United States Environmental Protection Agency's Environmental Monitoring Systems Laboratory – Las Vegas.

Notice

Although the information in this paper has been funded in part by the United States Environmental Protection Agency under contract number 68-03-3249 to Lockheed Engineering & Sciences Company, it has not been subjected to Agency review. It therefore does not necessarily reflect the views of the Agency and no official endorsement should be inferred. The mention of trade names or commercial products does not constitute endorsement or recommendation for use.

References

- Bivand, R. (1980) A Monte Carlo study of correlation coefficient estimation with spatially autocorrelated observations, *Quaestiones Geographical*, Vol. 6, No. 1, pp. 5-10.
- Brimblecombe, P., Tranter, M., Abrahams, P. W., Blackwood, I., Davies, T. D., and Vincent, C. E. (1985) Relocation and preferential elution of acidic solute through the snowpack of a small, remote, high-altitude Scottish catchment, *Annals of Glaciology*, Vol. 7, pp. 141-147.
- Cliff, A. D., and Ord, J. K. (1981) *Spatial processes: models and applications*, Pion Limited, London, 266 pp.
- Cragin, J. H., Giovinetto, M. B., and Gow, A. J. (1984) Baseline acidity of ancient precipitation from the South Pole, U.S. Army Cold Regions Research and Engineering Laboratory Report 84-15, 7 pp.
- Davies, T. D., Vincent, C. E., and Brimblecombe, P. (1982) Preferential elution of strong acids from a Norwegian ice cap, *Nature*, Vol. 300, No. 5883, pp. 161-163.
- Davison, W., and Harbinson, T. R. (1988) Transient responses of glass electrodes in dilute solutions and freshwaters, *Analyst*, Vol. 113, No. 10, pp. 1537-1540.
- Delmas, R. J., and Aristarain, A. (1978) Recent evolution of strong acidity of snow at Mt. Blanc, *Studies in Environmental Science*, Vol. 1, pp. 233-237.
- Delmas, R. J., and Gravenhorst, G. (1983) Background precipitation acidity, In: *Acid deposition*, ed. Beilke, S., and Elshout, A. J., D. Reidel, Dordrecht, pp. 82-107.
- Freund, J. E. (1971) *Mathematical statistics*, second edition, Prentice-Hall, Englewood Cliffs, pp. 197-199.
- Hess, B. C., Rocchio, J. E., Chaloud, D. J., Arent, L. J., and Engels, J. L. (1988) Wet deposition and snowpack monitoring: final project report, EPA/600/4-88/009, U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Las Vegas, Nevada, 125 pp.
- Holdsworth, G., and Peake, E. (1985) Acid content of snow from a mid-troposphere sampling site on Mount Logan, Yukon Territory, Canada, *Annals of Glaciology*, Vol. 7, pp. 153-160.
- Jenkins, M. D., Drever, J. I., Reider, R. G., and Buchanan, T. (1987) Chemical composition of fresh snow on Mount Everest, *Journal of Geophysical Research*, Vol. 92, No. D9, pp. 10,999-11,002.
- Johannessen, M., and Hendricksen, A. (1978) Chemistry of snow meltwater: changes in concentration during melting, *Water Resources Research*, Vol. 14, No. 4, pp. 615-619.
- Jones, H. G. (1985) The chemistry of snow and meltwaters within the mesostructure of a boreal forest snow cover, *Annals of Glaciology*, Vol. 7, pp. 161-166.
- Jumars, P. A. (1978) Spatial autocorrelation with RUM (Remote Underwater Manipulator): vertical and horizontal structure of a bathyal community, *Deep Sea Research*, Vol. 25, No. 7, pp. 589-604.
- Koerner, R. M., and Fisher, D. (1982) Acid snow in the Canadian high Arctic, *Nature*, Vol. 295, No. 5845, pp. 137-140.
- Kumai, M. (1985) Acidity of snow and its reduction by alkaline aerosols, *Annals of Glaciology*, Vol. 6, pp. 92-94.
- LaChapelle, E. R. (1969) *Field guide to snow crystals*, University of Washington Press, Seattle, p. 67.

Spatial Variability in Snow Chemistry

- Laird, L. B., Taylor, H. E., and Kennedy, V. C. (1986) Snow chemistry of the Cascade – Sierra Nevada Mountains, *Environmental Science and Technology*, Vol. 20, No. 3, pp. 275-290.
- Legrand, M. R., Aristarain, A. J., and Delmas, R. J. (1982) Acid titration of polar snow, *Analytical Chemistry*, Vol. 54, No. 8, pp. 1336-1339.
- Legrand, M., and Delmas, R. J. (1985) Spatial and temporal variations of snow chemistry in Terre Adelie (East Antarctica), *Annals of Glaciology*, Vol. 7, pp. 20-25.
- Metcalf, R. C. (1984a) The accuracy of pH determination in glacial melt waters, *Zeitschrift für Gletscherkunde und Glazialgeologie*, Vol. 20, No. 1, pp. 41-51.
- Metcalf, R. C. (1984b) Effect of storage solution composition on pH electrode response times at low temperature, *Analyst*, Vol. 109, No. 9, pp. 1225-1226.
- Metcalf, R. C. (1984c) Field pH determinations in glacial melt waters, *Journal of Glaciology*, Vol. 30, No. 104, pp. 106-111.
- Metcalf, R. C. (1987a) Accuracy of Ross pH combination electrodes in dilute sulphuric acid standards, *Analyst*, Vol. 112, No. 11, pp. 1573-1577.
- Metcalf, R. C. (1987b) A field procedure for accurate pH measurements in low solute content waters, In: Burt, T., *British Geomorphological Research Group Technical Bulletin No. 36*, Geo Books, Norwich, England, pp. 28-41.
- Metcalf, R. C., Stapanian, M. A., Hoenicke, R., Arent, L. J., Peck, D. V., Baker, J. R., and Kinney, W. L. (1988) Continuous electrochemical monitoring of snow melt in Utah, U.S.A., Proceedings of the Seventh Northern Research Basins Symposium /Workshop: Applied Hydrology in the Development of Northern Basins, Ilulissat, Greenland, Danish Society for Arctic Technology, Copenhagen, pp. 169-178.
- Metcalf, R. C., Peck, D. V., and Arent, L. J. (1989) The influence of dissolved organic carbon on pH measurements of low solute content waters, *Geochimica et Cosmochimica Acta*, Vol. 53, No. 4, pp. 773-784.
- Metcalf, R. C., Peck, D. V., and Arent, L. J. (1990) Effect of potassium chloride additions on pH measurements of dilute sulphuric acid standards, *Analyst*, Vol. 115, No. 7, pp. 899-905.
- Neftel, A., Moor, E., Oeschger, H., and Stauffer, B. (1985) Evidence from polar ice cores for the increase in atmospheric CO₂ in the past two centuries, *Nature*, Vol. 315, No. 6014, pp. 45-47.
- Oeschger, H., Schotterer, U., Stauffer, B. Haeberli, W., and Rothlisberger, H. (1977) First results from alpine core drilling projects, *Zeitschrift für Gletscherkunde und Glazialgeologie*, Vol. 13, No. 1-2, pp. 193-208.
- Rocchio, J. E., Metcalf, R. C., Reese, M., Todechney, L., Arent, L. J., Pierett, S. L., Baker, J. R., Chaloud, D. J., Reiner, R., and Reiner, L. (1988) Chemistry of Front Range snowfall, Rocky Mountains, Colorado, *Ice*, No. 86, p. 15.
- Rossum, J. R. (1975) Checking the accuracy of water analyses through the use of conductivity, *Journal of the American Water Works Association*, Vol. 67, No. 3, pp. 204-205.
- Schemenauer, R. S., Summers, P. W., Wiebe, H. A., and Anlauf, K. G. (1985) Spatial and temporal variability of surface snowfall and snowpack chemistry in central Ontario, *Annals of Glaciology*, Vol. 7, pp. 185-190.
- Schotterer, U., and Oeschger, H. (1981) Information stored in ice, In: *Switzerland and her glaciers, from the ice age to the present*, ed., Kasser, P., and Haeberli, W., Kummerly and Frey, Berne, p. 121.

- Thrush, S. F., Hewitt, J. E., and Pridmore, R. D. (1989) Patterns in the spatial arrangements of polychaetes and bivalves in intertidal sandflats, *Marine Biology*, Vol. 102, No. 4, pp. 529-535.
- Wolff, E. W., and Peel, D. A. (1985) The record of global pollution in polar snow and ice, *Nature*, Vol. 313, No. 6003, pp. 535-540.
- Zar, Z. H. (1984) *Biostatistical Analysis*, second edition, Prentice-Hall, Englewood Cliffs, pp. 653-656.

First received: 27 February, 1990

Accepted: 28 May, 1990

Address:

Environmental Programs Office,
Lockheed Engineering & Sciences Company,
1050 E. Flamingo Rd., Ste. 209,
Las Vegas, NV-89109.
U.S.A.