Soil solution chemistry at one mountain beech (*Fagus sylvatica* L.) CONECOFOR plot, 1999 to 2005

Guia Cecchini[1*], Stefano Carnicelli[1], Guido Sanesi[1]

Accepted 18 September 2007

Abstract – Soil solution monitoring aims to understand various temporal scales of soil processes. The first eight years of observation in ABR1 Level II site have brought significant elements of understanding about the shorter temporal scales. It is suggested that certain solutes, regularly produced by forest floor microbial processes, are transferred to the highly mobile portion of the soil solution by a non linear process, producing irregular pulses and creating a strong high frequency component. Seasonal processes remain nonetheless detectable after simple and rough filtering. A multi-year trend of diminished nitrate mineralization and increased pH of forest floor solutions is possible. It is estimated that much more accurate analysis will be possible in a relatively short time span of further monitoring.

Key words: *beech forest, soil solution, trends.*

Riassunto – Chimica della soluzione del suolo in un'area CONECOFOR montana di faggio nel periodo 1999-2005. Tra gli scopi del monitoraggio delle soluzioni circolanti del suolo c'è la comprensione delle diverse scale temporali dei processi. I primi otto anni di osservazione nel sito Livello II ABR1 hanno portato significativi elementi di comprensione rispetto alle scale temporali più brevi. Le osservazioni suggeriscono che certi soluti, regolarmente prodotti da processi microbici negli orizzonti organici, siano trasferiti alle soluzioni del suolo per mezzo di un processo non lineare, che produce pulsazioni irregolari e determina una forte componente ad alta frequenza nello spettro temporale. Ciò nonostante, gli andamenti stagionali restano individuabili con l'applicazione di un filtraggio molto semplice. I dati suggeriscono la possibilità di tendenze poliennali verso la diminuzione del flusso di nitrati e l'aumento del pH nelle soluzioni all'interfaccia organico-minerale. Si ritiene che un notevole miglioramento della possibilità di analisi dei dati sarà possibile dopo una ulteriore fase di monitoraggio di durata relativamente breve.

Parole chiave: *faggio, soluzione del suolo, tendenze temporali.*

F.D.C. 114.28: 524.634: 176.1 Fagus sylvatica

Introduction

The main value of continuous monitoring of soil solution composition rests in the ability to observe different scales of temporal trends in soil genesis, physiological, and chemical processes. However, such ability comes neither cheaply nor easily; multiple methodological obstacles are disseminated along the road and some measure of strength and patience is required of the researcher. Among the main methodological problems, we start from the need that a purposely designed solution sampler is properly placed. As purposely designed at it may be, the sampler is bound to disturb local soil environment. Gravity samplers, normally used below the forest floor, may alter rates of organic matter deposition and decomposition; tension samplers, normally used within the mineral soil, can produce preferential water flow paths, and always include an intrinsic ambiguity between free-flowing and weakly retained water. The proportions of these water fractions will vary with time, according to complex physical forcings. Spatial variability, especially when considering dynamic soil fluids over short time frames, may be up to extreme. Temporal variability, for how sought after it is, may be troublesome to handle. Temporal variability of soil solution composition realizes itself across a very wide span of scales, and it is often difficult to discriminate between the different components. The typically irregular, and low, sampling frequencies definitely

[1] Dipartimento di Scienza del Suolo e Nutrizione delle Piante. Università di Firenze Piazzale delle Cascine 45, 50144 Firenze, (Italy).
[*] Corresponding author: *guia.cecchini@unifi.it*

don't help. The main starting point to start disentangling these issues is to examine seasonal trends. This because we do have plenty of "physical" (as opposed to statistical) knowledge about the forces driving seasonal variations; this should help us to understand apparent trends, even when data amount is not up to rigorous statistical standards. Seasonal variations may eventually be strongly covariant with other "noise" sources, such as soil water content and rate of water flux through soil. This is partly a double-edged sword, as effects may show up in a bundled form and be difficult to separate, but again solid physical bases about processes and factors promise help.

This paper reports the exploratory analyses of soil solution chemistry for ABR1 site, with the goal to start building an understanding of seasonal trends and related sampling issues. The aim is to assess minimum requirements concerning time span and data density for the development of effective algorithms for separating the components of the time spectrum of soil solution composition, to allow isolation of meaningful multi-year trends.

Methods

Soil solution sampling in ABR1 station started in 1999 (Cecchini *et al.* 2002), with additional support from previous research. Presently, data are available until 2005, giving a temporal baseline over which an exploratory evaluation is possible. On the other hand, it must be kept in mind that the sample base amounts to only 74 samples; just to set the scales, this number of samples is equivalent to about 2 years of deposition sampling, and insufficient to apply suitable advanced statistical analysis as found in Spangenberg and Bredemeier (1999) or Stein and Sterk (1999). Gravity samplers in ABR1 were renewed in fall 2004, as part of the normal procedure required by "ageing" of such samplers; this adds to the complexity of the task. The set of solution samplers is the one prescribed by ICP manuals, and routine ICP quality control procedures are performed on the results; this includes regular participation to solution chemistry ring tests, organized by both ICP and by NIVA. General site and soil characteristics are described in Cecchini *et al.* (2002). Data obtained by previous researches are also examined, as relevant to the issue of sampler "ageing" effects.

Results

For initial data exploration, a summary analysis of overall parameter variability and dynamics was applied, comparing of the different sampler sets. From such rapid assessment it was evident how forest floor samplers produce the data set which are of most interest for time series analysis.

Various concomitant factors make this happen. In bio-physical terms, forest floor reacts to environmental variations faster than any other soil compartment, reflecting in the high dynamics of all solution parameters. Previous, single event-based, analyses (Cecchini *et al.* 2002) showed how solutions from forest floor samplers often register analyte concentrations one or two orders of magnitude higher with respect to all other soil solution samplers, notwithstanding the fact that they see the largest water flow. This suggests that, for the time scales accessible here, forest floor processes are capacious enough to "swamp" other processes, and that behaviour of lower horizons may be, at this stage, approximated as a response to forest floor inputs.

In data processing terms, forest floor phenomena are likely to show the most tractable problems of time delay between driving (precipitation, climatic, phenological) factors and response. The possibility to assume small and constant time delays should be quite useful in establishing general trends of seasonal behaviour, to be used as a reference to evaluate time delay issues in lower horizons. In statistical terms, forest floor provides the most uniformly distributed sampling time intervals and the highest data density in time, both factors of great help in time series analysis.

Examination of data from individual sampling times tends to support the interpretations put forward in Cecchini *et al.* (2002). The driving variables of soil solution equilibrium still appear to be the supply of nitrate anion, produced within the forest floor by litter decomposition, and the balancing availability of basic cations, of partly external origin. These interactions bear heavily on such fundamental soil solution properties as pH and EC.

According to this process-oriented analysis, a small set of parameters were selected for detailed statistical analysis. These include pH, EC, Nitrate and Sulphate; this last analyte was selected as a shorthand indicator of total external dust supply (Cecchini *et al.* 2002).

As a first step, parameters were plotted versus time (Figure 1). Even if a few irregularities spoil visual evidence, seasonal trends look rather clear. Nitrate con-

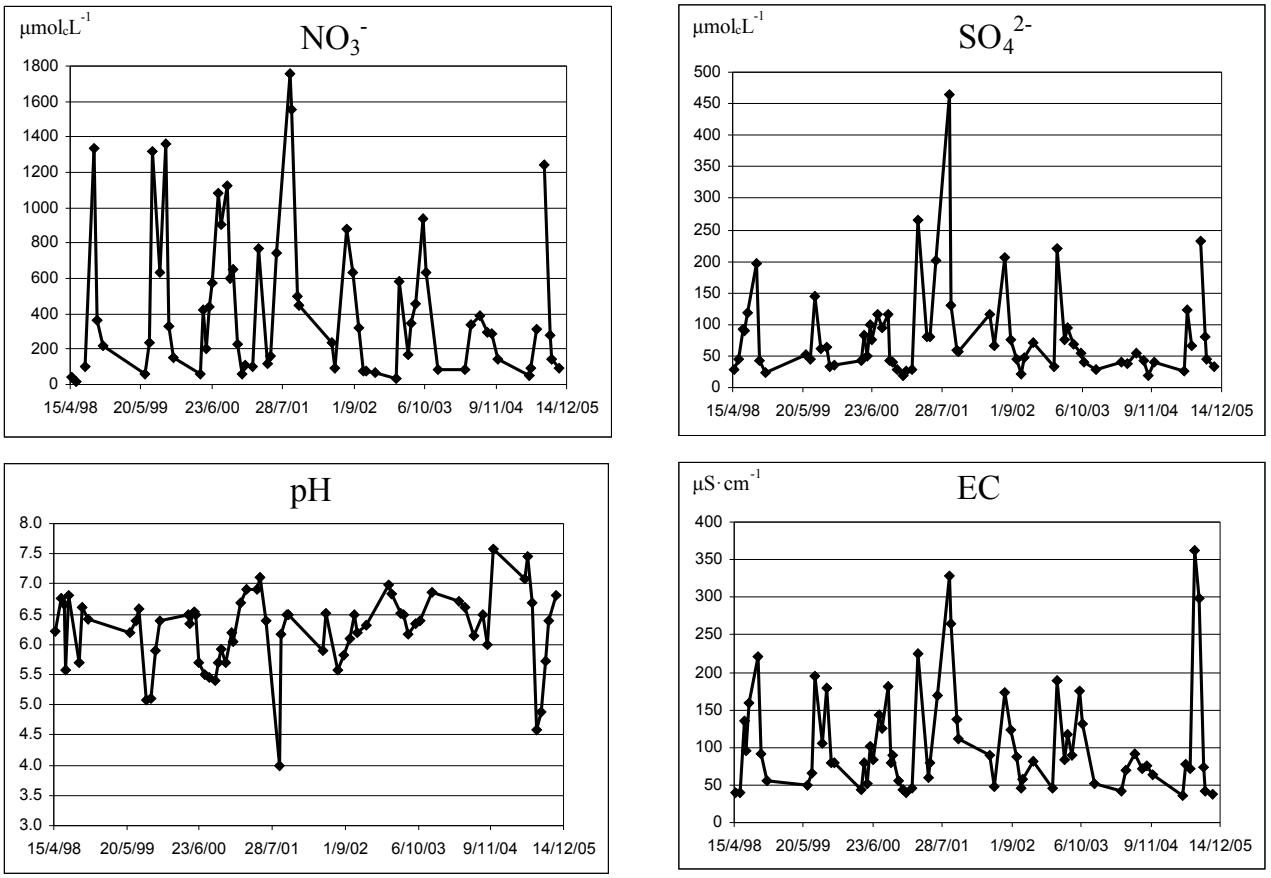


Figure 1 - Time series of selected soil solution parameters.
Serie temporali di parametri selezionati delle soluzioni del suolo.

centration peaks in summer months; in some cases, a well defined "fork" aspect is visible, with an early summer peak, a decrease and then a second peak, in late summer or, sometimes, in early fall.

EC follows nitrate values very closely. Sulphate follows the same general trend, but not as closely; in particular, the summer "fork" is not evident; pH appears less regular, but a closer look, and consideration of measurement uncertainties, suggests an essentially stable value, broken by sudden, short-term, drops, typically in summer.

If these seasonal trends are clear, use of simple, strictly chronological, detrending tools is barred by small irregularities in actual dates, so that "early summer" varies from late June to late July, "late summer" from mid-August to early October, and so on. Logically, it is the actual climatic sequence for each individual year that determines the exact position of peaks and valleys. A climatically-based detrending tool is expected within the next few years, when a somewhat larger base of data will become available.

The large measure of agreement between these parameters, as summarized in Figure 2, prompted a regression analysis for the main parameter pairs. Such analysis evidenced how both nitrate and sulphate are significantly correlated with EC, while pH definitely is not (Figure 3).

This suggests EC as a potential scale for detrending of both nitrate and sulphate values. Such suggestion has a physical base; in summer conditions, reduced water flux may obviously be responsible for increased concentrations of analytes. However, such a concept model would imply the assumption that nitrate flux from solid phase to solution is essentially constant, what is definitely unlikely. As rate of litter decomposition should vary greatly, on a seasonal basis, under

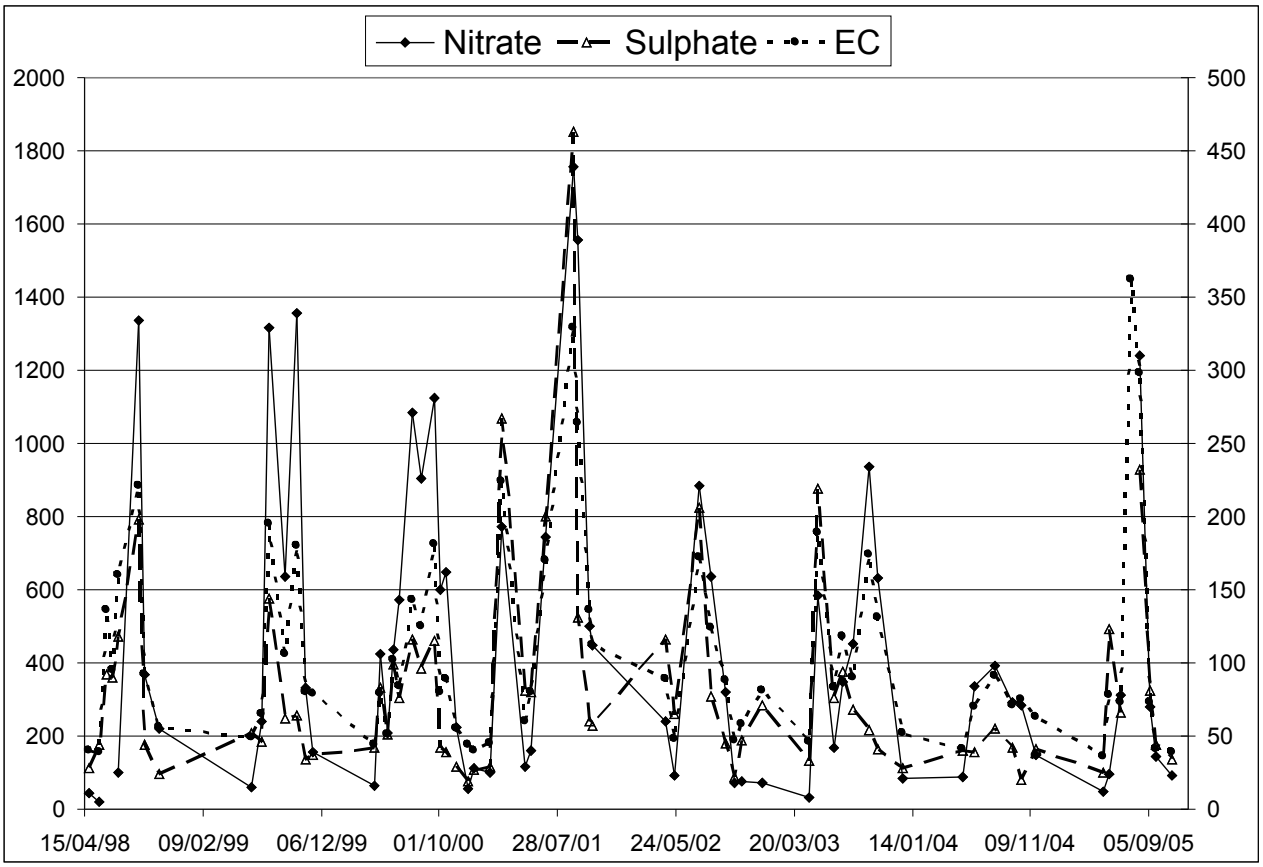


Figure 2 - Joint time series of Nitrate, Sulphate *in µmol$_c$L^{-1} (left axis)* and EC *in µS·cm^{-1} (right axis).*
Serie temporali di Nitrato, Solfato e Conducibilità Elettrica (EC); Nitrato e Solfato in µmol$_c$L^{-1} (scala a sinistra); EC in µS·cm^{-1} (scala a destra).

the influence of temperature and moisture, summer peaks are clearly enhanced by faster mineralization under warmer temperature. However, mineralization rate should undergo a slow change, and cannot explain the strong high-frequency component that is evident in most raw analyte time series. To produce this kind of temporal variation, it is more or less necessary to call into play some specific process of forest floor solution mobilization, depending on water flow.

A second set of interactions to be considered concerns the secondary effects of high nitrate concentrations on other solution parameters. Total ion strength of soil solutions is upper bound by the availability of conjugate bases (Ugolini and Sletten 1991). Nitrate is the most important conjugate base in these solutions, then its concentration could be a major factor in controlling release of cations. The causal relation between nitrate and EC should then work both ways, and detrending according to EC is too severe.

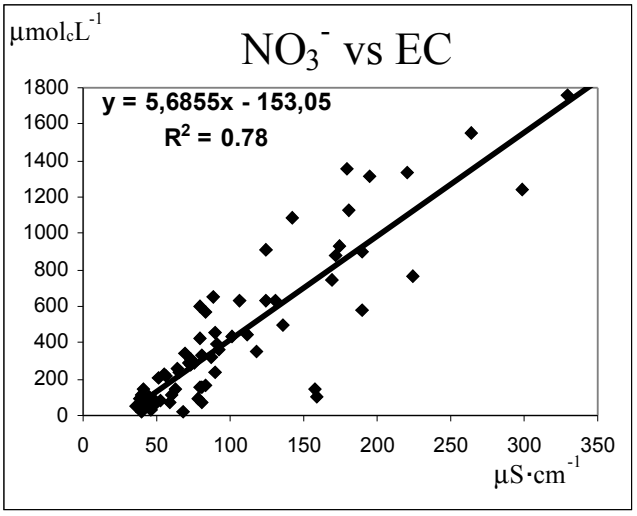
From this initial evaluation of the complexity of the interactions involved, we conclude that more complex and truly efficient detrending algorithms need to be developed, based on broader bases of data and that, for the time being, it is sensible to interpret together a "raw" time series of nitrate and sulphate concentrations and a "detrended" one, obtained by calculating the difference between measured concentrations and those estimated by the regression equation on EC. Compared, raw and detrended, time series for nitrate and sulphate are shown in Figure 4.

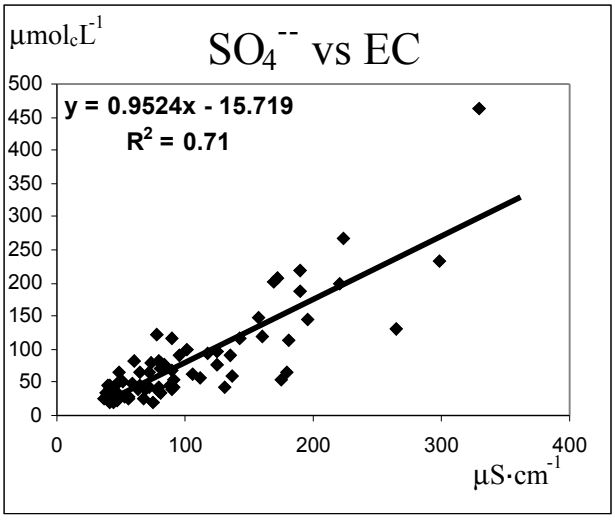
It appears very clearly that detrending by EC does not completely suppress seasonal trends; this is a good result, implying that the method is not physically absurd. We can infer, from this results, that the seasonal trends evident in "raw" data, and consistent with process knowledge, are also strong enough to survive an excessively severe detrending treatment. They can then be considered as a safe base for further understanding.

A divergence of possible interpretations yet arises

concerning prospective long-term trends. Raw data suggest a multi-year trend of nitrate decrease that, however, could well be a sampling artefact. The presence of very high peaks in both 1999-2001 and 2005 would suggest that high nitrate release can be a reaction to the disturbance caused by inserting the samplers. The early peak would have been followed by progressive normalization in 2002-2003 and the return to high nitrate output been caused by the new samplers. When looking at the detrended data, however, we observe that the values in both 1997-1998 and 2005 could be not so different from 2002-2004, true nitrate peaks being those of 1999-2001. Further argument for a physical long-term trend comes from the observation that, while the first "disturbance peak" would have showed up with a significant delay after installation, the 2005 one would have been quite immediate, suggesting that the same physical processes are not at work in the two cases. Decreasing nitrate release from the forest floor could then be a robust long-term trend, following a 1999-2001 peak. Linked to this could be another apparent trend, a slow rising pH of the forest floor solution (fig. 1). These ambiguities will anyway be resolved in the next few years of observations. These should also build up a long enough pH time series, as the present one is too small with respect to the skewed and high-kurtosis distribution of the values, limiting usable statistical techniques.

Comparison of detrended data shows that covariance between nitrate and sulphate is only broad and does not hold at this level of detail; this is a further support for the hypothesis that a major sulphate input is not from organic matter mineralization, but rather from atmospheric pollution and/or dust, as previously supposed (Cecchini *et al.* 2002).





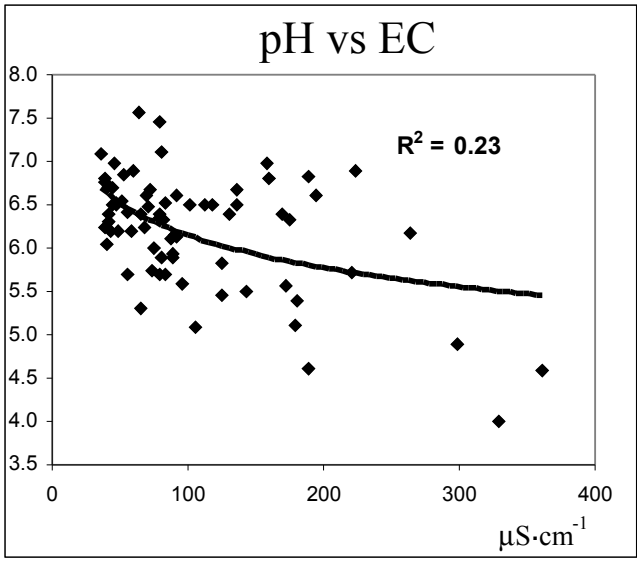


Figure 3 - Regressions of Nitrate, Sulphate and pH on EC.
Regressioni di Nitrato, Solfato e pH sulla EC.

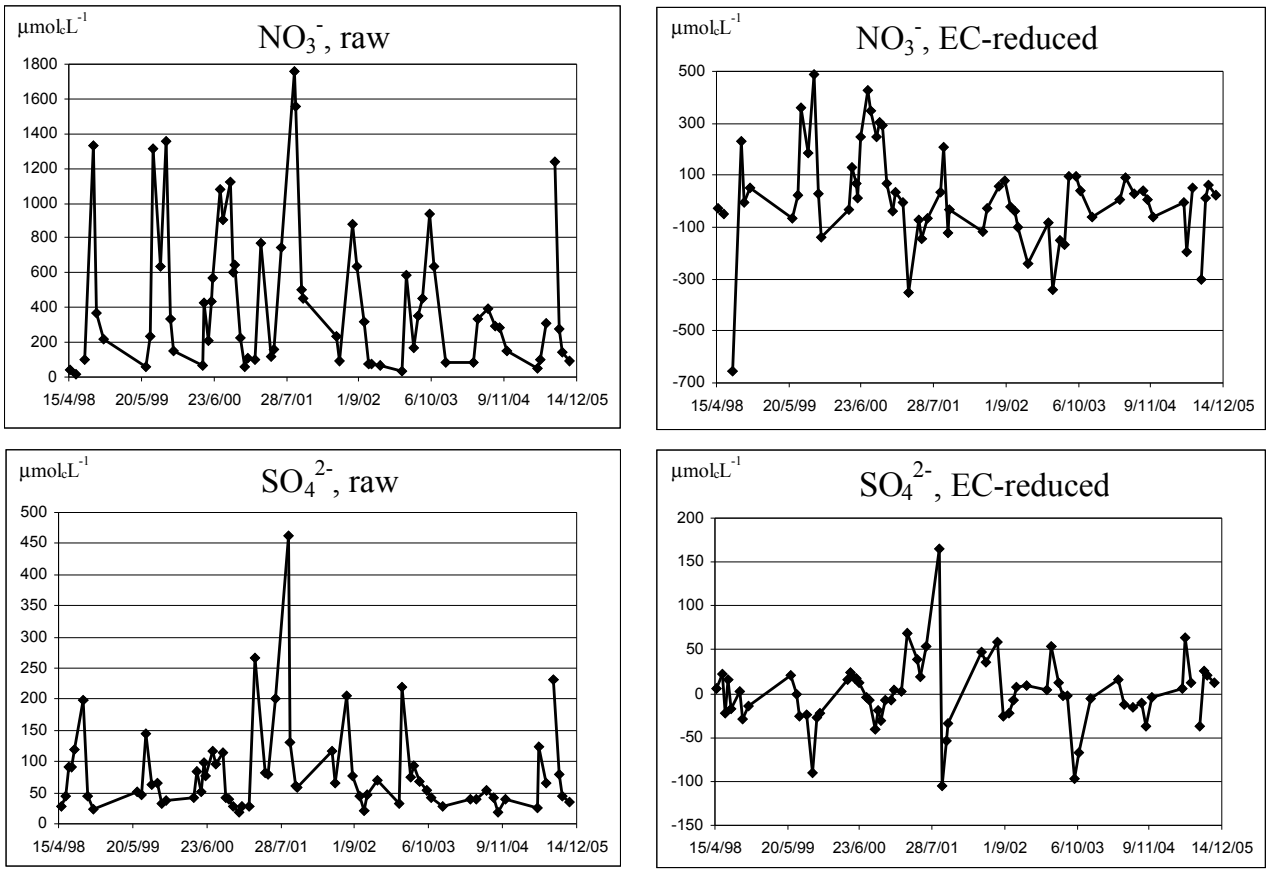


Figure 4 - Comparison of unprocessed and EC-reduced time series.
Confronto tra serie temporali grezze e ridotte in base a EC.

Conclusions

Soil solution monitoring requires a long-term effort to build up a base of data large enough to overcome many serious limitations to statistical analysis. Nevertheless, the first eight years of monitoring in ABR1 station are revealing various significant knowledge. The basic elements of the interplay between processes that produce the most important solutes and those that otherwise control their movement are beginning to be revealed. The need of further data is clearly defined, and likely to be met within a few years.

References

Cecchini G., Carnicelli S., Mirabella A., Mantelli F., Sanesi G. 2002 - *Soil conditions under a Fagus sylvatica CONECOFOR stand in Central Italy: an integrated assessment through combined solid phase and solution studies.* In: Mosello, R., B. Petriccione and A. Marchetto (guest editors): Long-term ecological research in Italian forest ecosystems. J. Limnol., 61 (Suppl. 1): 36-45.

Spangenberg A., Bredemeier M. 1999 - *Application of spectral analysis to meteorological and soil solution chemistry data.* Chemosphere, 39 (10): 1651-1665.

Stein A., Sterk. 1999 - *Modeling space and time dependence in environmental studies.* J. Appl. Earth Obs. and Geoinformation, 1 (2): 109-121.

Ugolini F.C., Sletten R.A. 1991 - *The role of proton donors in pedogenesis as revealed by soil solution studies.* Soil Sci., 151: 59-75.