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Relationships between spruce plantation age, solute and soil chemistry in Hafren forest

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Abstract

Rain, throughfall, soil waters from surface peaty O horizon and deeper mineral B horizon, and stream water, were collected every four weeks for one year in a moorland catchment, and in four forested catchments. The four forested catchments represented an age sequence of first rotation Sitka spruce plantations, aged 14, 28, 37 and 53 years. All water samples were analysed for all major solutes, including dissolved organic nitrogen (DON-N); stream water and B horizon soil waters were also subjected to aluminium speciation. In each catchment, soil samples were collected on one occasion and pH was measured.

Concentrations of most solutes were substantially higher in the 37 year old forest stand than in the moorland catchment, with intermediate concentrations in the two younger stands and 53 year old stand. In particular, higher nitrate-N concentrations were found in the soils and streams of the older forests, although these concentrations tended to be highest in the 37 year old stand. Acid neutralizing capacity (ANC) of soil waters was lower in the B horizon of the forest stands than in the moorland, and tended to decline with increasing forest age. Soil water from both O and B horizons was most acid in the 37 year old stand, and the water from the soil O horizon in all four forest stands was more acid than that in moorland sites. The pH of the soil itself (as measured in a deionised water slurry) was lower in the forest stands than in moorland, although trends with forest age were complex.

Introduction

In the uplands of Wales, a number of studies have linked coniferous afforestation with acidification of soil and stream water (e.g. Stoner and Gee, 1985; Reynolds *et al.*, 1988; Ormerod *et al.*, 1989). A key mechanism driving this process is the enhanced capture of atmospherically-derived particulate, cloud droplet and gaseous materials by the conifer canopy (Fowler *et al.*, 1987), but depletion by tree uptake of the soil base cation store also contributes to soil acidification (Reuss and Johnson, 1986). Of the materials captured by the canopy, and which are subsequently washed into the soil, dry deposition of the oxides of sulphur and nitrogen (SO₂ and NO_x) contribute directly to soil and potentially to stream water acidity once dissolved in water. Of the natural atmospherically derived materials, sodium chloride from sea-salt, brought in during strong westerly winds, causes pulses of soil and stream water acidification through cation exchange by Na of H ions held in the acid soils of upland Wales (Soulsby, 1995).

During the late 1980s, the balance of interest concerning deposition and the acidification of soils and streams shifted from the role of SO₂ to that of nitrogen compounds (Grennfelt and Hultberg, 1986; Skeffington and Wilson,

1988). Evidence that certain forest ecosystems were becoming 'nitrogen saturated' was emerging from Scandinavia (Henriksen and Brakke, 1988), N. America (Aber *et al.*, 1989) and also Wales (Emmett *et al.*, 1993; Stevens *et al.*, 1993). The evidence from Wales consisted of input-output balances of dissolved nitrogen for a mature, 50 year old Sitka spruce (*Picea sitchensis* (Bong.) Carr.) plantation in Beddgelert forest. Output of nitrogen in the stream amounted to 14.6 kg ha⁻¹ year⁻¹, almost entirely as nitrate-N at an average concentration of 0.78 mg l⁻¹. In contrast, inputs in bulk precipitation were only 10.3 kg ha⁻¹ year⁻¹, of which approximately equal amounts were nitrate-N and ammonium-N. It was also clear that nitrification, which is an acidifying process, was active in the soils of this forest (Stevens and Wannop, 1987). In streams draining younger Sitka spruce plantations in Wales, nitrate-N concentrations were lower—0.23 mg l⁻¹ at Llyn Brianne where the trees were 22 to 24 years old (Stoner *et al.*, 1984), and 0.39 mg l⁻¹ at Plynlimon where the trees ranged from 21 to 40 years old. In non-forested, agriculturally-unimproved upland catchments at Plynlimon, nitrate-N concentrations were lower at 0.15 to 0.17 mg l⁻¹ (Reynolds *et al.*, 1992).

These observations on a limited number of catchments suggested that, as Sitka spruce plantations age, they gradually become nitrogen saturated, and this is demonstrated as enhanced nitrate concentrations in soil solution and streams. This forest age relationship was observed in data collected during the 1984 Welsh Water 'Acid Waters Survey of Wales' (Reynolds *et al.*, 1994) and, to examine the relationship further, a study of 25, mainly forested, catchments throughout upland Wales was initiated to examine the nitrogen inputs, outputs and throughputs in relation to plantation age, a study known as the 'Forest Nitrogen Survey' (Hughes *et al.*, 1994; Stevens *et al.*, 1994). The study confirmed a trend of increasing nitrate-N concentrations and leaching with increasing stand age. The predominant soil type within these catchments was a stagnopodzol, which is a free draining type in which nitrification occurs freely, producing nitrate-N (in contrast, nitrification is not likely to be important in poorly draining soils such as gleys and peats). Five of the catchments used for the 'Forest Nitrogen Survey', representing an age sequence of moorland and Sitka spruce plantations 14, 28, 37 and 53 years old, were located within, or immediately adjacent to, Hafren Forest at Plynlimon. This paper presents previously unpublished data from these five catchments, especially in relation to seasonal trends in concentration of nitrogen species, and examines the influence of forest age on the extent and causes of soil and stream acidification.

Site and Methods

The catchments were selected using the following criteria:-

- the five catchments should include one in semi-natural moorland, and one in each of four forest ages categories—0–15, 16–30, 31–45 and 45 plus years.
- underlying geology should be Ordovician/Silurian shale or mudstone.
- they should be dominated by stagnopodzol soils such that any variation due to soil type could be eliminated,
- plantations should be first rotation
- each catchment should be as 'pure' as possible as regards the age of plantations present, i.e. as much as possible

of the catchment should carry trees within the required age band.

Details of these catchments are shown in Table 1. Only in one case, the moorland catchment, otherwise known as C2, has any other detailed study been undertaken of the stream chemistry (Reynolds *et al.*, 1983; 1992). The moorland catchment is dominated by acid grasslands composed mainly of *Festuca*, *Agrostis* and *Nardus*, which are believed to have existed in the four forested catchments prior to afforestation. There is no known history of agricultural 'improvement' in the moorland catchment, or in any of the forested catchments prior to afforestation,

The 14, 28 and 53 year old forests were unthinned, and in the case of the two younger stands, the canopies were complete and dense. The canopy of the 53 year old stand, however, was showing signs of becoming gappy, and considerably less dense than the 14 and 28 year old stands, possibly because of aphid damage and/or physical abrasion during gales. In contrast, the 37 year old stand had been line thinned, probably around five years previously, but the canopy of this stand had effectively closed again and was dense and complete.

Samples of bulk precipitation, throughfall, soil waters from the surface peaty O horizon and sesquioxide-enriched illuvial B horizon, and stream water were collected approximately every four weeks from November 1990 to October 1991 in each catchment. The throughfall and soil waters were obtained from a single 20m by 20m plot within each catchment, and these plots were located within representative areas of moorland or forest, as appropriate. Throughfall in the forest sites was obtained using 12 collectors per site located at random along a 20 metre transect within the 20m by 20m plot. Each throughfall collector consisted of a 58 cm² polythene funnel and 5 litre polythene bottle supported such that the rim of the funnel was approximately 60 cm above the ground surface. The volumes of throughfall were measured and the 12 individual samples per site were bulked on each sampling occasion prior to analysis. At the moorland site, throughfall was collected by three sets of three lengths of miniature guttering inserted beneath the grass 'canopy', discharging into buried 5 litre bottles. Soil water from the peaty O

Table 1. Catchment characteristics.

	Moorland	Forest, 14 years old	Forest, 28 years old	Forest, 37 years old	Forest, 53 years old
Grid reference of stream sampling point.	SN 818842	SN 844807	SN 822882	SN 869849	SN 845861
Altitude of stream sampling point (m)	430	480	580	380	400
General aspect (degrees)	10	20	120	100	60
Catchment area (ha)	4	2	1	32	6.5
Mean tree height (m)	—	5.1	7.1	14.9	12.5
Stand basal area (m ² ha ⁻¹)	—	16.2	25.2	48.4	39.5
Thinning	—	Unthinned	Unthinned	Line thinned	Unthinned

horizon was obtained from three simple PVC tensionless lysimeters per site, each discharging into buried 10 litre carboys, with the three samples per site being bulked prior to analysis on each sampling occasion. Water samples from the B horizon were obtained from each site using three porous ceramic cup suction samplers, similar to those described by Wagner (1962). The three samples per site were bulked prior to analysis on each sampling occasion. Bulk precipitation was collected from suitably open areas close to or within the catchments using a 15cm diameter PVC funnel and bottle assembly.

All water samples were returned to the laboratory where pH was measured on an unfiltered sub-sample. Other major solutes—Na, K, Ca, Mg, Cl, $\text{SO}_4\text{-S}$, $\text{NO}_3\text{-N}$, $\text{NH}_4\text{-N}$, DON (dissolved organic-N) and DOC (dissolved organic carbon) were analysed by conventional techniques after filtering the remaining sample through 0.45 micron filters. Aluminium speciation of the soil and stream waters was carried out according to the scheme of Driscoll 1984. Full details of field sampling procedures and chemical analyses are provided in Stevens *et al.* (1994) and Hughes *et al.* (1994). Calculations of volume-weighted mean concentrations in bulk precipitation and throughfall for the year utilised actual volumes of water in the appropriate collection bottles. For the soil waters and streams, mean concentrations for the year were weighted using estimates of soil water flux for each four-week period obtained as the difference between throughfall inputs and evapotranspiration losses, the latter being calculated using a modified Penman-Monteith equation applied to data from a local automatic weather station (described in Emmett *et al.* (1993)).

Samples of soil were collected on a single occasion from the peaty O, eluvial E, illuvial B and parent material transition zone (C horizon) from three pits excavated in representative locations in each of the five catchments. The pH was measured on the four horizon samples from each pit individually using de-ionised water ($\text{pH}_{\text{H}_2\text{O}}$ —10g moist soil, 25 ml water) and CaCl_2 ($\text{pH}_{\text{CaCl}_2}$ —10g moist soil, 25ml 0.01M CaCl_2), and the mean for each horizon from each site calculated.

Results

VARIABILITY IN ANNUAL DISSOLVED-N CONCENTRATIONS BETWEEN CATCHMENTS

Weighted mean concentrations of the three dissolved-N species varied substantially, not only by stratum (i.e. rain, throughfall, soil, streams), but also with land use (moorland, forest) and forest age (Figure 1). Concentrations in rain were very similar at all five sites, however, and differences in rain concentrations can be discounted as a cause of variation in concentration in the other strata. In the moorland catchment, highest dissolved-N concentrations were in throughfall (contamination from animal exc-

reta is possible, although not observed), and concentrations decreased progressively through the O and B horizons to the stream. In the moorland stream, dissolved-N concentration was only 30% that in rain and it is clear, even in the absence of a nitrogen budget for this catchment, that this moorland system is immobilising nitrogen. This is also occurring in three of the forest sites, but most noticeably in the 14 year old stand.

In the forest catchments, dissolved-N concentrations in throughfall increased with stand age from 14, through 28 to 37 years old, but in the oldest stand, concentrations were similar to those in the 28 year old stand. Enhanced capture of dry deposited NO_x and NH_3 in the older stands is likely, although the mature 53 year old stand had a less complete canopy than either the 28 or 37 year old stands, a feature apparently reflected in the lower dissolved-N concentration in throughfall in this case.

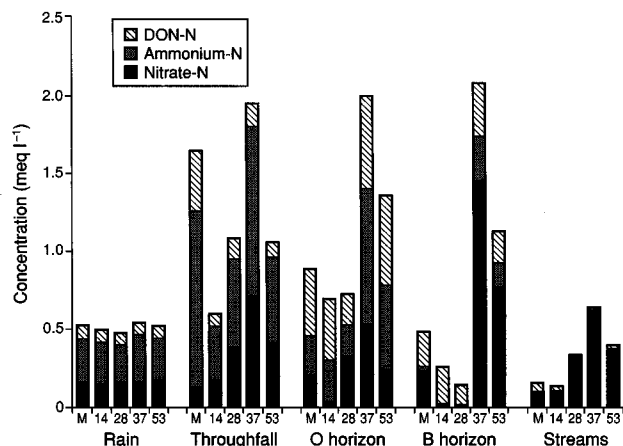


Fig. 1. Volume-weighted annual mean concentrations (mgN l^{-1}) of nitrate-, ammonium- and dissolved organic-N (DON-N) in rain, throughfall, O and B horizon soil water, and streams in moorland (M) and forested catchments (14, 28, 37 and 53).

A relationship with stand age which is stepped, rather than linear, is also observed in the soil and stream water chemistry. In the soil O and B horizons, the sites tend to group into the moorland, 14 and 28 year old forest stands with lower dissolved-N concentrations, and the 37 and 53 year old stands with higher concentrations. In the streams, the differences are less marked, but concentrations in the moorland and 14 year old stand were similar and low, whereas in the 28, 37 and 53 year old stands, higher concentrations were present.

Concentrations of dissolved-N in the B horizon of the 14 and 28 year old stands were lower than in the O horizon, indicating that root uptake of nitrogen had occurred from the zone between these horizons. In contrast, in the older two stands, concentrations were very similar in both O and B horizons, so root uptake was either negligible in

these stands in the zone between the O and B horizons, or was balanced by larger rates of mineralisation of N in this zone in the older two stands.

A striking feature of the data in Figure 1 is the change in the proportions of the three nitrogen species as water passes through these systems; stream water in all five catchments was dominated by nitrate, as were the B horizons of the older forest stands. Nitrate and ammonium-N were virtually absent from the younger forest B horizons, whereas in throughfall and O horizon waters there was a much more even division. In rain, nitrate and ammonium-N dominated the total dissolved-N concentrations.

SEASONAL VARIATION IN DISSOLVED-N CONCENTRATIONS

The weighted mean concentrations shown in Figure 1 were calculated for the one-year period of this study. They hide substantial temporal variability in the data. For example, Figures 2, 3 and 4 show that nitrate-N concentrations varied through the year in the streams, B horizon soil waters and throughfall respectively in the five catchments. In all but the 14 year old catchment, stream nitrate-N concentrations were lowest in late spring to early autumn, although variability was not large and appeared somewhat damped in the forest catchments. The trend observed in the moorland catchment is well established at Plynlimon (Reynolds *et al.*, 1992). This winter peak of nitrate-N may be derived either from mineralisation and subsequent nitrification of soil organic-N, or may simply be nitrate deposited from the atmosphere leaching through, or both. In summer, the available nitrate-N is immobilised through plant uptake; in winter, there is no such sink.

Nitrate-N concentrations in the streams draining the 28, 37 and 53 year old forests remained higher than those in the moorland stream throughout the year (Figure 2) and plant uptake and immobilisation of N in these forests is clearly unable to contend with the quantities of nitrogen available, even during the growing season. However, annual stream concentrations for the 28 and 53 year old stands compared to rainfall concentrations imply net retention. These data indicate that a larger proportion of the incoming nitrogen is immobilised in the moorland system than in these forests, which allow a significant proportion of the nitrogen to leach out.

Stream chemistry data from this study are not altogether straightforward to interpret, since the results are the integration of the influences of the entire catchment. Although great efforts were made to ensure that, for instance, forest age and management were uniform across any one catchment, this was virtually impossible to achieve, and small areas of different forest types were inevitably present. The influence of riparian zones and their diverse vegetation was also impossible to quantify. Consequently, it is the soil waters and throughfall which should provide even more appropriate evidence of the effects of the different forest ages.

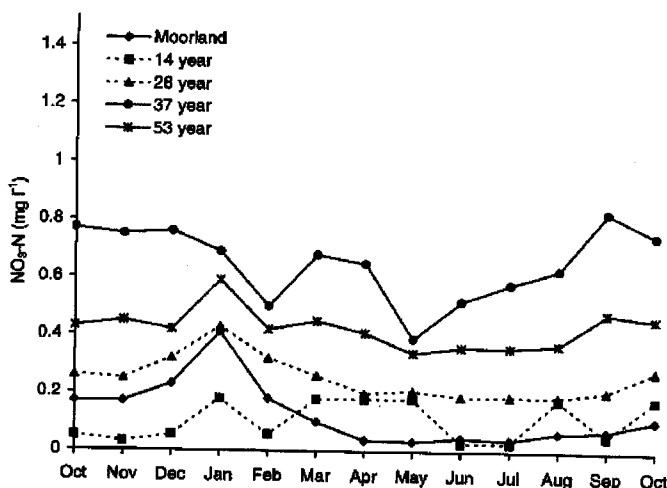


Fig. 2. Variation in nitrate-N concentrations (mg N l^{-1}) with time during the period October 1990 to October 1991 in streams draining moorland and forested catchments.

The most striking features of the B horizon soil waters were the pronounced seasonal trends in nitrate-N in the 37 and 53 year old forest stands (Figure 3). Highest concentrations were in summer, the opposite to the trend in the moorland catchment. Clearly, nitrate production occurs in these Welsh stagnopodzols, and in the older forests quantities of nitrate appear to be in excess of the demands of the vegetation and other sinks, resulting in accumulation in the soil in summer (Figure 3) until washed out to streams by autumn rainfall (Figure 2).

In contrast to these older stands and moorland, nitrate-N was virtually undetectable in the B horizon of the two younger forests, and throughout the year (Figure 3). This is understandable in summer, when biomass uptake will be

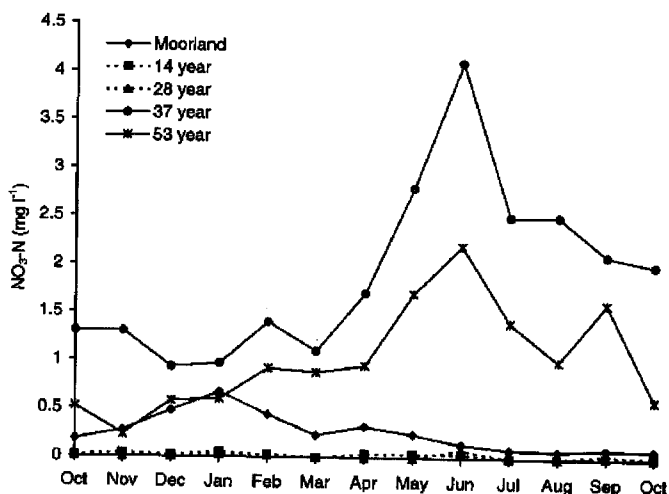


Fig. 3. Variation in nitrate-N concentrations (mg N l^{-1}) with time during the period October 1990 to October 1991 in B horizon soil water from moorland and forested catchments.

active, but the lack of any nitrate in winter is surprising. It is clear from the moorland data (Figure 3) that nitrate is normally present in B horizon soil waters in winter, so an unknown sink for nitrate-N is presumably active. This could be denitrification, but this seems unlikely since there is no reason why this should be active in the soils of these younger stands and not in the moorland or older stands. Alternatively, biomass uptake of N could be occurring, even in winter, in the young stands. The winter of 1990/1991 was remarkably mild and it is recognised that Sitka spruce has a long growing season with the ability to increase biomass and continue root growth through UK winters (Cannell, 1987). An alternative explanation is that the soil microbial population, which is active throughout the year, is unable to compete with tree uptake during the growing season, becoming nitrogen stressed. During the winter, when the trees stop or slow their growth, this microbial population takes the opportunity to restore its nitrogen status by utilising the available nitrate, which consequently remains at very low concentration in the soil solution.

The variation over time in nitrate-N in the B horizon and streams is unlikely to be linked directly to variation in concentration in atmospheric inputs in throughfall, since seasonal trends in the latter were negligible (Figure 4). The pattern in Figure 4 is characterised by spikes of much higher concentration standing out from a comparatively uniform baseline, especially in the older two stands, but no apparent seasonal component. The spikes represent large concentrations, but only small inputs of N, since they correspond with low rainfall months. In fact, there were significant negative relationships ($p < 0.05$) between monthly nitrate-N concentration and monthly throughfall amount in the 14, 37 and 53 year old stands, and this relationship was very significant ($p < 0.01$) in the 28 year old stand and moorland. The spikes of nitrate-N in throughfall are

unlikely to influence the soil water chemistry since the small volumes of water associated with them will not have penetrated far into the soil.

VARIATION IN CONCENTRATION OF THE OTHER MAJOR ANIONS AND CATIONS

Considerable variation in the concentrations of the major anions and cations with stratum, land use and forest age is apparent from Figures 5 and 6. Figure 5 reveals the variability in nitrate-N already described, but also its comparative insignificance as a component of the total anion concentration. A forest age effect is apparent, such that the total inorganic anion concentration (nitrate plus sulphate plus chloride) in throughfall, O horizon and B horizon soil waters increased from the 14 to 37 year old stand, and then dropped in the oldest stand. In the 37 year old stand, the total inorganic anion concentration in throughfall, O horizon, B horizon and stream was 4, 6, 7 and 3-fold that in incoming rain, and points to the immense influence of the canopy in enhancing deposition inputs, especially of sulphate and chloride. In contrast, the effect of concentration of solutes resulting from evapotranspiration, which is rarely more than 50% of incident rainfall in spruce plantations, is unlikely to be responsible for more than a two-fold increase. Predictably, cations (Figure 6) show similarly enhanced concentrations in throughfall and soil waters, compared with rain. Sodium (for clarity not shown in Figure 6) matched increased chloride concentrations very closely. Magnesium and calcium concentrations in throughfall were 4 to 5 fold those in rain, and in the case of magnesium, this degree of enhancement was apparent in soil waters and streams. With calcium, however, concentrations in soil water were lower than in throughfall, indicating that root uptake, cycling and canopy leaching of this cation occurs in a similar manner to potassium (Parker, 1983). Stream calcium concentrations were substantially larger than those in soil water, although still relatively low, implying that sources of calcium are present in these catchments beneath the soil cover, possibly as calcite mineralisation in the bedrock.

Hydrogen ion concentrations also showed considerable variability. Soil waters were the most acid, with the O horizon more acid than the B horizon. Age-related trends were apparent, although only marked in the B horizon and throughfall, with the 37 year old stand the most acid (O horizon pH 3.8, B horizon 4.2), whereas the moorland was the least acid (O horizon pH 4.3, B horizon pH 4.5). Throughfall in the two older stands was noticeably more acid than rain, by 0.4 to 0.5 of a pH unit, whereas throughfall under the two younger stands was similar to that in rain. In complete contrast, throughfall beneath the moorland grass canopy was less acid than in rain (pH 5.5 and 4.8 respectively); this is probably not an anomalous result, since a similar difference was observed at four other moorland sites in Wales at the same time.

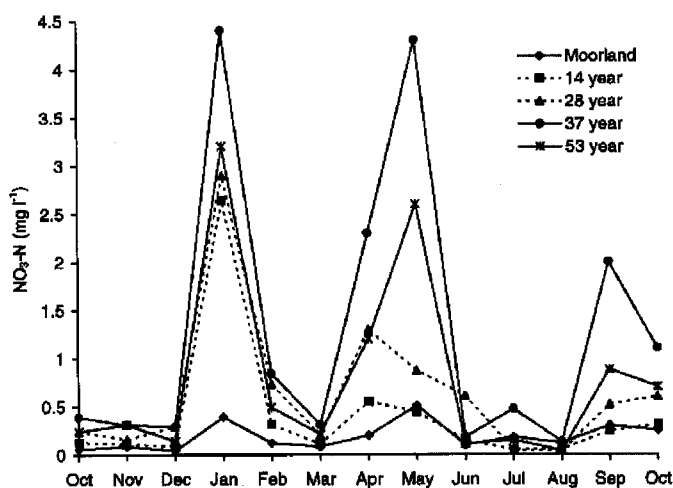


Fig. 4. Variation in nitrate-N concentrations (mg N l^{-1}) with time during the period October 1990 to October 1991 in throughfall from moorland and forested catchments.

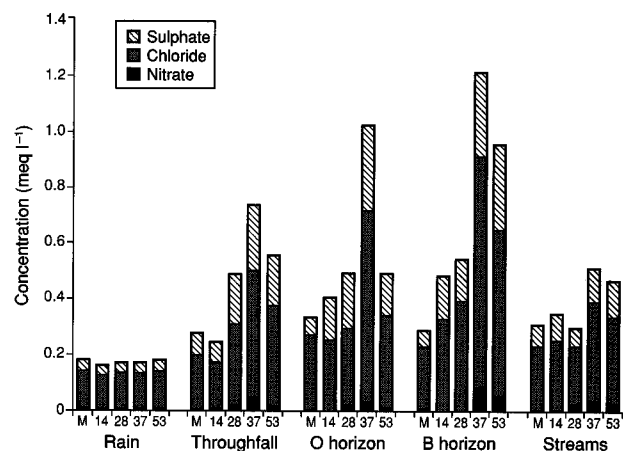


Fig. 5. Volume-weighted mean concentrations (meq l⁻¹) of nitrate, chloride and sulphate in rain, throughfall, O and B horizon soil water, and streams in moorland (M) and forested catchments (14, 28, 37 and 53) for the year October 1990 to October 1991 inclusive.

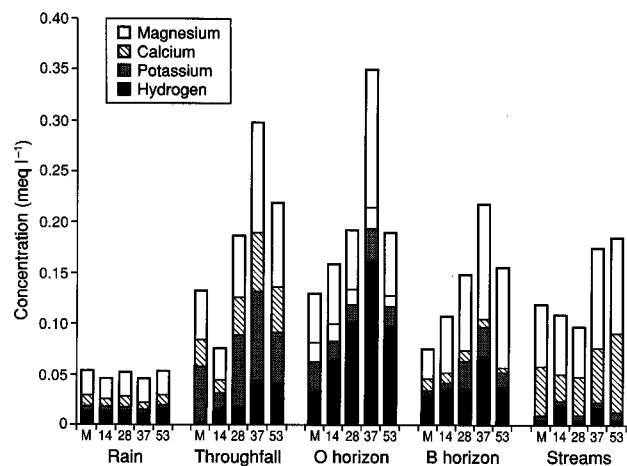
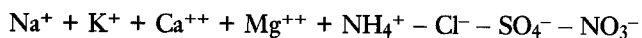


Fig. 6. Volume-weighted mean concentrations (meq l⁻¹) of hydrogen ion, potassium, calcium and magnesium in rain, throughfall, O and B horizon soil water, and streams in moorland (M) and forested catchments (14, 28, 37 and 53) for the year October 1990 to October 1991 inclusive.

SOIL ACIDITY

It has been clearly demonstrated in Figure 6 that soil waters beneath conifer plantations were more acid than soil waters of comparable moorland sites, and that the most extreme values were found in the 37 year old stand. Also demonstrated in Figure 6 is the lack of such a relationship in the streams draining these forests. In waters, acid neutralising capacity (ANC) may be used as an indicator of acid-base status, and has been calculated here from annual volume-weighted mean concentrations as:-



ANC values were all negative (Figure 7), apart from moorland throughfall. Soil waters had the largest negative values, and an age relationship was again apparent, in particular in the B horizon. In contrast with the results for individual anions and cations (Figures 5 and 6), the B horizon of the 53 year old stand showed the largest negative ANC, although the O horizon ANC of this stand had a smaller value than either the 28 or 37 year old stands. As with pH, there was no relationship between stream water ANC and forest age.

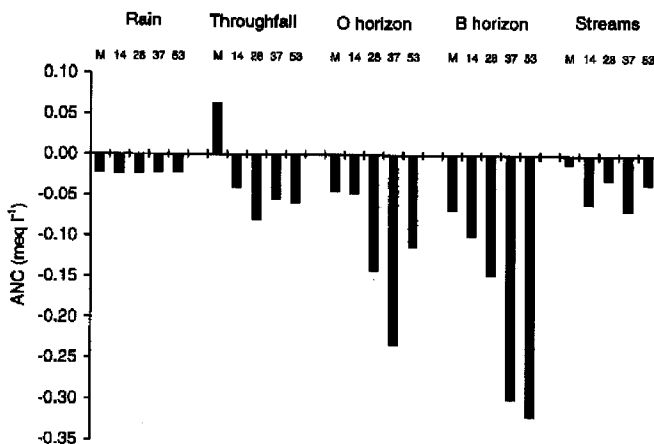


Fig. 7. Acid neutralizing capacity (ANC) in rain, throughfall, O and B horizon soil waters, and streams in moorland (M) and forested catchments (14, 28, 37, 53) for the year October 1990 to October 1991 inclusive.

Acidification of soils under conifer plantations is also apparent, not only by soil waters, but by the soil itself. In Figure 8, the mean soil pH_{H₂O} values are shown for each of the four major horizons of the stagnopodzol and each of the five sites. At all sites, pH_{H₂O} was lowest in the peaty surface O horizon, but there was also a marked trend of decreasing pH in all horizons from moorland to forest, and with increasing stand age in the E horizon. In the soil of the 53 year old stand, pH_{H₂O} in the O, E, B and C horizons was 0.14, 0.23, 0.30 and 0.21 units lower respectively than in the equivalent horizons of the moorland soil.

For pH_{CaCl₂} values were lower in the forests than in the moorland (Figure 9), but there was no evidence of the age-related trend seen for pH_{H₂O} in the E horizon; in fact, pH_{CaCl₂} increased in three of the four horizons with increasing forest age. The difference between pH values obtained in water or CaCl₂ slurries is not unexpected, since the use of the latter is normally advocated as a means of obtaining consistent results in situations where there is variation in solution ionic strengths; this is the case in the soil solutions in this study, in which higher total anion and cation concentrations were observed, especially in the soil waters of the 37 year old stand. The higher cation concentrations will result in H ions being displaced from

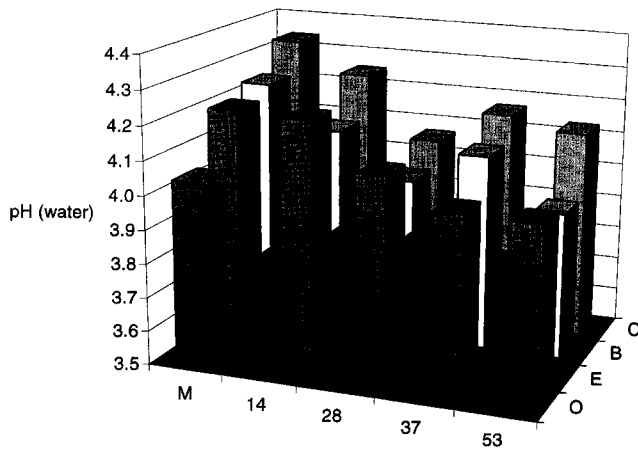


Fig. 8. Soil pH (measured in water) from O, E, B and C horizons from moorland (M) and forested catchments (14, 28, 37, 53).

exchange sites into solution causing a lowering of solution pH and soil $\text{pH}_{\text{H}_2\text{O}}$. The latter may therefore be regarded as the 'true' soil pH, since it is the pH prevailing under ambient concentrations of other solutes, whereas $\text{pH}_{\text{CaCl}_2}$ provides an indication of pH 'normalised' to uniform solute concentrations.

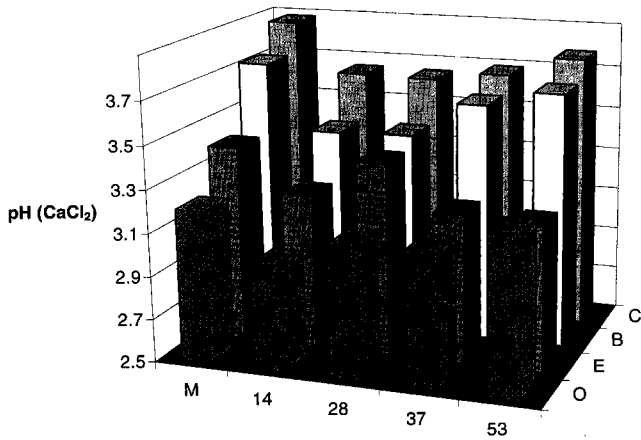


Fig. 9. Soil pH (measured in CaCl_2) from O, E, B and C horizons from moorland (M) and forested catchments (14, 28, 37, 53).

SPECIATION OF ALUMINIUM

Despite the mixed evidence for acidification of soils with increasing forest age, there is no question that the soil solution of the 37 year old stand was more acid than in the moorland and younger plantation soils. High concentrations of major solutes were present in the soil waters of the 37 year old stand and in the B horizon; this was also the case for aluminium. Speciation of this aluminium reveals it to be predominantly in the labile monomeric form (Figure 10), even in the surface peaty O horizon, where a larger proportion could be expected to occur as non-labile

aluminium-organic complexes. In the streams, labile monomeric aluminium was also predominant, although concentrations were much lower than in the B horizon, and there was no convincing effect of the forest, or of forest age. The weighted mean annual concentrations ranged from 0.04 mg l^{-1} in the moorland stream, to 0.45 mg l^{-1} in the stream draining the 37 year old plantation, although maximum concentrations measured in individual monthly samples were 0.08 and 0.65 mg l^{-1} in these two streams respectively. Maximum concentrations of labile monomeric aluminium in the streams were in winter, and the seasonal trend was particularly marked in the forest catchments (Figure 11). In the B horizon soil waters, the trends were less clear, with late-winter peaks but a rather less marked summer trough (Figure 12).

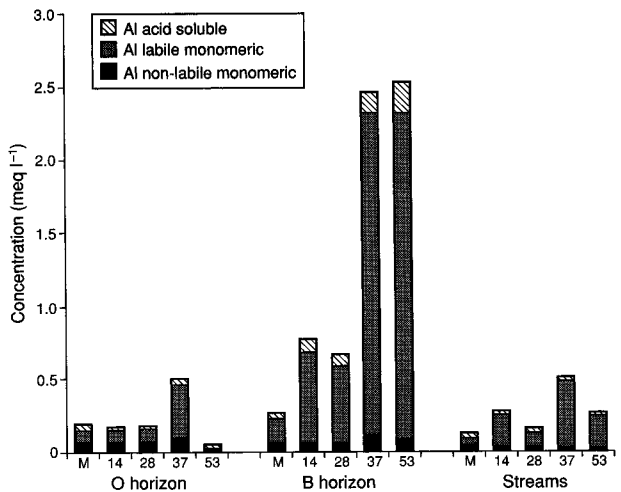


Fig. 10. Volume-weighted mean concentrations of aqueous aluminium, fractionated according to Driscoll, 1984, in O and B horizon soil solution and streams from moorland (M) and forested catchments (14, 28, 37, 53) for the year October 1990 to October 1991 inclusive.

RELATIONSHIPS BETWEEN SOLUTES

The concentration of labile monomeric aluminium in these acid soil and stream waters is likely to be related to their pH and concentrations of other ions. Results from correlation analysis of the major solutes in the streams (Table 2) and B horizon (Table 3) reveal that these relationships are confirmed in some cases but there is intriguing variability between catchments, and between soil water and stream water. Where correlations were highly significant, the reason is that the solutes concerned show similar seasonal trends. In streams, labile monomeric aluminium concentrations were highest in winter (Figure 11) and there is also good reason to expect that the marine-derived solutes Na, Cl and Mg should also show a similar trend. However, there was surprisingly large variability in the relationships between labile monomeric aluminium and these ions

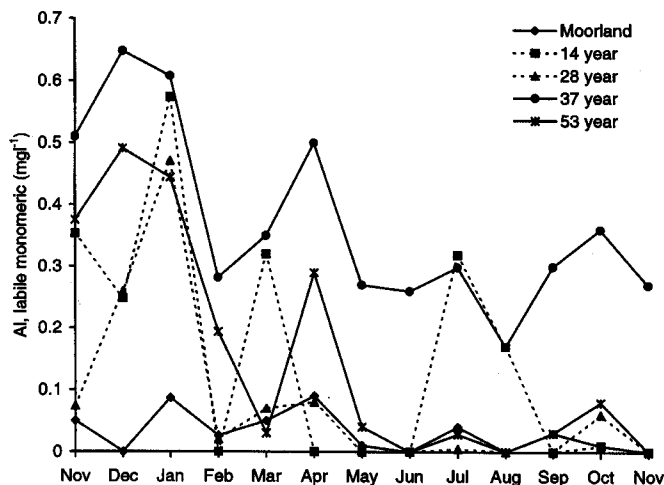


Fig. 11. Variation in labile monomeric aluminium concentrations with time during the period from October 1990 to October 1991 in streams.

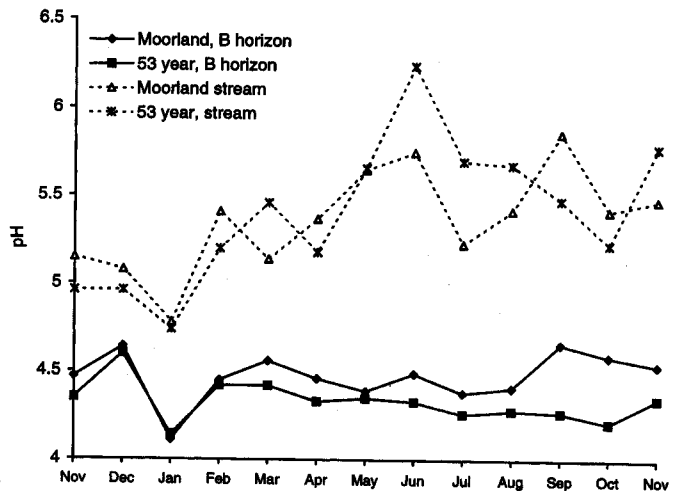


Fig. 13. Variation in pH with time during the period October 1990 to October 1991 in B horizon soil waters and streams in the moorland and 53-year old forest catchments.

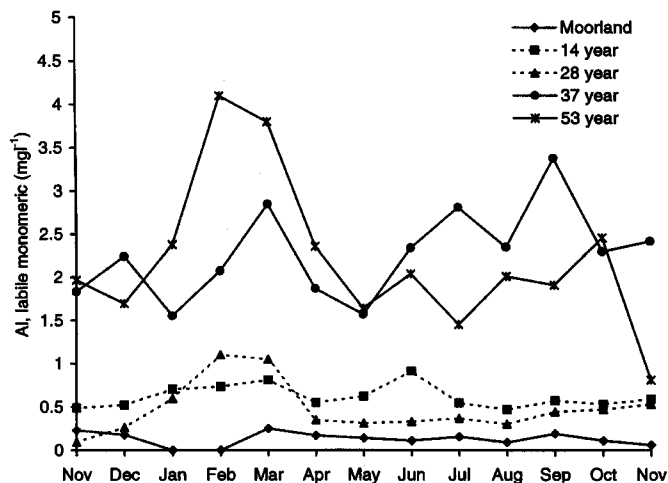


Fig. 12. Variation in labile monomeric aluminium concentrations with time during the period from October 1990 to October 1991 in the B horizon soil waters.

(Tables 2 and 3); these cannot be explained readily, and their relationships with nitrate-N were either not significant, or only marginally so at $p < 0.05$.

Stream pH (Figure 13) was lower in winter, as a result of a larger proportion of stream water being routed only through the upper soil, and 'salt events' (Soulsby, 1995). A good correlation between labile monomeric aluminium and H ion would be expected and this was indeed true for four of the five streams, but not for the soils, where pH did not vary much during the year (Figure 13). Indeed, in soil waters, the main source of variation in pH as shown in Figure 13 was presumed to be a prolonged salt event, corresponding with a period of three weeks of very wet, westerly weather prior to the January 1991 sampling. The

data presented in Figure 13 also indicate that the pH of the streams draining the moorland and 53 year old stands were little different, and showed a similar response to the salt event.

Discussion

Stream water chemistry has been characterised extensively for the Plynlimon catchments, especially in relation to the contrast between moorland and afforested catchments, assessment of variability, long term trends and the impacts of clearfelling (e.g. Durand *et al.*, 1994; Neal and Hill, 1994; Neal *et al.*, 1989; 1990; 1992; 1994; Reynolds *et al.*, 1992; Robson *et al.*, 1992a). Temporal variability in individual streams may be attributed to season (in summer, streams are dominated by high alkalinity baseflow) or short term, event-related episodes with high sea-salt concentrations. Differences between the mean chemistries of streams may be attributed to geological and soil variability, forest cover, and clearfelling of mature forest stands. Considerable success has also been achieved in modelling and predicting chemical variability in the major streams draining the Plynlimon catchments—the Hafren, Hore, Gwy, Cyff, (e.g. Neal *et al.*, 1992; Robson *et al.*, 1991; 1992b; 1993).

The current study confirms conclusions from earlier studies (e.g. Reynolds *et al.*, 1988; Stoner and Gee, 1985) that soil and stream waters in afforested catchments are characterised by higher concentrations of aluminium and other major solutes than in moorland streams, although afforested catchments are not necessarily characterised by lower pH. Furthermore, the forest influence has been shown to be progressive, especially in the soil B horizon, with positive relationships having been established between forest age and solute concentration, although a

Table 2. Correlation coefficients for labile aluminium concentrations with other major solutes in stream water. Significance levels are * = $p < 0.05$, ** = $p < 0.01$, *** = $p < 0.001$.

	Moorland		14 year		28 year		37 year		53 year	
H	0.57	*	0.60	n.s.	0.96	***	0.61	*	0.91	***
Na	0.54	n.s.	0.87	**	0.81	***	0.09	n.s.	0.20	n.s.
K	0.83	***	-0.33	n.s.	0.14	n.s.	-0.25	n.s.	-0.03	n.s.
Ca	-0.07	n.s.	0.83	*	-0.62	*	-0.79	**	-0.74	**
Mg	0.34	n.s.	0.84	*	0.68	**	-0.53	n.s.	-0.50	n.s.
Cl	0.66	*	0.85	*	0.90	***	0.50	n.s.	0.56	*
SO ₄ -S	-0.36	n.s.	-0.49	n.s.	-0.07	n.s.	-0.49	n.s.	-0.60	*
NO ₃ -N	0.42	n.s.	0.22	n.s.	0.32	n.s.	0.51	n.s.	0.34	n.s.
DOC	-0.18	n.s.	-0.57	n.s.	0.01	n.s.	0.43	n.s.	0.21	n.s.

Table 3. Correlation coefficients for labile aluminium concentrations with other major solutes in B horizon soil water. Significance levels are * = $p < 0.05$, ** = $p < 0.01$, *** = $p < 0.001$.

	Moorland		14 year		28 year		37 year		53 year	
H	-0.20	n.s.	0.05	n.s.	0.27	n.s.	0.42	n.s.	-0.13	n.s.
Na	0.63	*	0.14	n.s.	0.71	**	-0.48	n.s.	0.81	***
K	-0.22	n.s.	-0.42	n.s.	-0.28	n.s.	-0.63	*	-0.03	n.s.
Ca	0.61	*	0.75	**	0.75	**	-0.65	*	0.38	n.s.
Mg	0.70	**	0.58	*	0.87	***	-0.49	n.s.	0.84	***
Cl	0.65	*	0.35	n.s.	0.87	***	-0.02	n.s.	0.88	***
SO ₄ -S	0.07	n.s.	0.19	n.s.	-0.74	**	-0.61	*	-0.24	n.s.
NO ₃ -N	0.56	*	0.23	n.s.	0.29	n.s.	0.58	*	-0.14	n.s.
DOC	0.03	n.s.	-0.49	n.s.	-0.61	*	-0.14	n.s.	-0.57	*

'tailing-off' of the effect is noticeable in the oldest stands. These relationships between forest age and stream chemistry may be attributed directly to processes occurring within the canopy and soils of these stands. These processes may be summarised as:-

1. enhanced deposition of atmospherically-derived particulate and gaseous material through dry and occult deposition (Na, Cl, Mg, SO₄-S, NO₃-N, NH₃, NO_x, Ca, K)
2. increased rates of cycling of nutrients by tree uptake, canopy leaching and litterfall, decomposition and root uptake (K, Ca, N)
3. changes in the rate or nature of soil processes: faster rates of nitrification in the soils of the older (>30 years) forest stands (Emmett *et al.* 1993), and consequent effects such as acidification.

These three processes interact with changes in the demand for nutrients as the trees grow older. For instance, demand for nitrogen by the younger, rapidly aggrading forests is substantial, but declines in older stands. In consequence, available nitrogen in solution in the younger stands is found at much lower concentration in the soil

than in older stands. Dissolved organic nitrogen mineralises to ammonium-N, which is readily taken up by the younger stands, together with any ammonium- and nitrate-N arriving in throughfall. Where ammonium and nitrate-N (from whichever source) are in excess of plant requirement, nitrifying bacteria in the soil will readily convert ammonium-N to nitrate-N, which will be readily leached into watercourses.

An additional factor to be considered is the effect of thinning. In the four stands described, only the 37 year old was thinned, with one in four rows of trees removed approximately five years prior to this study. The authors are unaware of any studies of the effects of forest thinning on soil and stream water chemistry, but it is likely that a pulse of nitrate would be produced in a similar manner to that generated after clear-felling (Stevens and Hornung, 1988;1990; Neal *et al.*, 1994). This thinning effect may therefore explain the higher nitrate concentrations in the 37 year old stand than in the other stands, and especially in the 53 year old stand. On the other hand, in the 37 year old stand after thinning, an increase in biomass and uptake of nutrients may have occurred as the canopies of the remaining trees expanded to fill gaps. The relative balance

between these sources and sinks of available nitrogen in the period after thinning remains unclear, but evidence from the study of 25 sites (Stevens *et al.*, 1994) indicates a similar 'dropping-off' of nitrate concentrations in the oldest stands, even where these have been thinned.

The combined effect of nitrification and subsequent leaching of the nitrate created is a process which will result in acidification of the soil. Soil acidification would therefore be predicted in the circumstances described in these Hafren Forest plantations, where enhanced nitrate-N leaching is shown to occur in older stands (Figure 1). The data presented here indicate that this is not entirely the case. Soil pH, especially when measured in water slurry, was noticeably lower in the forest stands than in the moorland, and the effect was evident throughout the soil profile (Figure 8), but the effect of forest age was not clear. Soil water from the B horizon clearly showed an effect of forest age, however; this is displayed convincingly by the decline in ANC, especially in the soil B horizon, which was substantially lower in the 37 and 53 year old stands than in the moorland or younger two stands. A similar trend was clearly evident for pH in throughfall and the soil waters, although, in these cases, the 37 year old stand was the most acid. The link between increased nitrate concentrations and soil acidity, as expressed by soil water aluminium concentrations, remains uncertain, however, since there was no relationship between aluminium and nitrate concentrations.

The acidification of the soils under coniferous forestry is a matter of continuing concern, not only because of the implications for stream water quality (although not clearly demonstrated by the original data), but for the long-term sustainability of the soils themselves. The study described here represents only the first forest rotation in what is intended to be an indefinite sequence. Clearly, the results from a single set of five sites at Plynlimon alone do not provide adequate evidence that soil acidification may be occurring on a wide scale, but data from other areas of Wales suggest it may (Emmett *et al.*, 1993; Hughes *et al.*, 1994; Stevens *et al.*, 1994). And if soil acidification is occurring in these forests, it will be the result of base cation uptake and immobilisation in tree biomass and accumulated forest floor tree litter, enhancement of the atmospheric inputs by the tree canopy, and the combined acidifying influences of nitrification and nitrate leaching.

Changes in forest management may be necessary to eliminate problems associated with nitrification and nitrate leaching. Single-aged stands require little nitrogen in their later stages. A more natural age structure containing a mix of tree ages (and species) would ensure a nitrogen sink in the form of younger trees would always be present, thereby eliminating the ammonium-N source for the nitrifiers. Such a management system would also eliminate the problems associated with the clearfelling phase.

Soil acidification resulting from biomass uptake of base cations would remain as a potential problem, depending

upon the overall balance of inputs versus outputs, unless amelioration were undertaken. It is unlikely that weathering rates of base cations in the soils of upland Wales would be adequate to replenish those base cations removed in harvested timber, but enhanced inputs of base cations from the atmosphere could potentially balance harvesting losses. The exact magnitude of net base cation inputs remain difficult to establish however, since modelling of these is difficult and contentious, and throughfall estimates contain a canopy leaching component which is even more difficult to quantify.

The future role of acidic pollutants in further soil acidification remains uncertain. Despite substantial reductions in SO₂ emissions, it is clear that throughfall and soil water concentrations of sulphate-S are three-fold those in moorland systems, and there is no reason to expect a change in this ratio even if SO₂ emissions decline further. The lower concentrations of sulphate-S in streams than in throughfall and soil waters also points to retention of sulphate-S in the forest soils, which is quite possible in podzolic soils, but sulphate-S held in this way may not be fixed permanently. The role of nitrogen in the acidification of upland soils must also be regarded as serious, as there is no indication at present of any major reductions in emissions being achieved.

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