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Nutrient Enrichment

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EXECUTIVE SUMMARY

The supply of macro-nutrients (nitrate, ammonia, phosphate and silicate) is the key driver of nutrient conditions in shelf seas. Increases in nutrient inputs above normal levels for an area can lead to a variety of deleterious effects, including oxygen depletion and mortalities of benthos and fish. Changes in the ratio of nitrogen or phosphorus to silicate in nutrient inputs can also affect the marine food web by altering the balance between diatom and other taxa in the phytoplankton community.

Nutrient inputs to shelf seas come from river inflows, rainfall and particulate deposition from the atmosphere, direct discharges of effluent to the sea, and from the open ocean as a result of currents and mixing. In some of these inputs the nutrient is essentially a natural component, and in others an anthropogenic load. Natural components include land erosion, global volcanic activity, lightning in the atmosphere, and ocean upwelling. Anthropogenic loads derive from urban waste water, agriculture, industry and fossil fuel combustion. Nitrogen and phosphorus inputs originate from both natural and anthropogenic sources, whilst silicate inputs are almost exclusively from natural processes. Current world patterns suggest that anthropogenic nutrient inputs are increasing, while inputs to European seas may be decreasing due to legislation designed to reduce emissions.

The waters around the UK are subject to a wide variety of terrestrial and anthropogenic nutrient inputs, and a range of exposures to oceanic exchange. In general, nutrient conditions in northern shelf waters are most influenced by ocean exchange, whilst terrestrial and anthropogenic inputs are more important in southern UK waters.

Climate change may affect the magnitude of natural inputs due to changing ocean upwelling and currents, and changing patterns of rainfall over the land catchments. Climate change may also affect the patterns of anthropogenic inputs, primarily through rainfall patterns and the effect on river flows. Disentangling trends in nutrient concentrations due to changing climate, human populations and industrialisation, and relating these to eutrophication status which is the major policy issue relating to nutrients, is a major scientific challenge.

FULL REVIEW

Introduction

The supply of macro-nutrients (nitrate, ammonia phosphate and silicate) is a key driver of biological production of shelf seas. Increased nutrient inputs relative to natural rates can lead to a variety of effects on the food web, some of which may be regarded as beneficial and others potentially deleterious, such as oxygen depletion and mortalities of benthos and fish.

Nutrient inputs to shelf seas come from rivers, rainfall and particulate deposition from the atmosphere, direct discharges of effluent to the sea, and from the open ocean as a result of currents and mixing (Hydes *et al.,* 1999, 2004). In some of these inputs the nutrient is essentially a natural component, and in others an anthropogenic load. Natural components include land erosion, global volcanic activity, lightning in the atmosphere, and ocean upwelling. Anthropogenic loads derive from urban waste water, agriculture, industry and fossil fuel combustion. Current world patterns suggest that global anthropogenic nutrient inputs to the sea are increasing, though in Europe the emissions of nutrient to river catchments are generally decreasing due to more stringent legislation since the 1970s (Carstensen *et al*. 2006; OSPAR 2003). However, there is evidence that changes in the flux of nutrient from some continental European estuaries to the sea have been buffered against changes in emissions to catchments due to the storage and biogeochemistry of nutrient in estuarine sediments (Soetaert *et al*. 2006; Vanderborght *et al*., 2007).

Climate change may affect the magnitude of natural inputs due to changing ocean upwelling and currents, and changing patterns of rainfall. Climate change may also affect the patterns of anthropogenic inputs, primarily through rainfall patterns and the effect on river flows. Disentangling trends in nutrient concentrations and eutrophication due to changing climate, human populations and industrialisation, is a major scientific challenge.

Sources of nutrient

Variations in nutrient loads of rivers are complex and have been described in a series of papers published in the journal "Biogeochemistry" in 1996; see Nixon *et al.* (1996), OSPAR documents (OSPAR, 2000), and a special issue of Limnology and Oceanography (Bachmann *et al*., 2006). There is significant research effort on river inputs both on a global scale (e.g. Jones *et al.* 1998; Dumont *et al.* 2005), European scale (Breton *et al*., 2006, Cugier *et al*., [Q2]2005a, Lancelot *et al*., 2007, Radach and Patsch, 2007, Vermaat *et al.,* 2008) and at the UK scale (e.g. Wilby *et al*., 2006) with work on specific catchments. Atmospheric inputs are particularly difficult to measure, and assessments are provided by the Cooperative Programme for Monitoring and Evaluation of the Long-range Transmission of Air pollutants in Europe (EMEP).

In general ammonia inputs derive mainly from human activities, and less from natural biogeochemical processes. Nitrate and phosphate inputs also derive from human activities, particularly agriculture and the discharge of sewage waters, but also from land erosion processes including loss of soil due to physical disturbance (e.g. in agriculture) and physical and chemical weathering of rocks, which are functions of rainfall, temperature (and the freeze-thaw cycle) and of CO_2 in water permeating rock. North Sea-wide, atmospheric deposition of nitrogen as ammonia is around half that as nitrate. Ammonia constitutes an even smaller fraction of nitrogen load in river inputs; around one-tenth of nitrate load North Sea-wide.

For the North Sea as a whole, nitrate input from rivers is approximately 4-times that from the atmosphere. However, there is large regional variation. At salinities less than about 34 the main source of nitrate is from rivers. Above a salinity of 34 in shelf waters, atmospheric inputs and mixing of ocean water onto the shelf have an increasing influence on nitrate concentrations. In the offshore northern North Sea the NE Atlantic is by far the largest source of nitrate, and is an important source in UK coastal waters, especially around the north of the UK (Vermaat *et al*., 2008).

Unlike ammonia, nitrate and phosphate, inputs of silicate to the sea are almost exclusively via river waters, and originate from the weathering of rock minerals. The only significant anthropogenic source of silicon is in urban waste water and originates from washing powders.

Biogeochemical processes

Nitrogen is rapidly recycled in the marine ecosystem by biological processes. Photosynthetic algae assimilate nitrate or ammonia for growth. When they are eaten by herbivores, a fraction of the nitrogen that was bound as organic material in the algae is excreted as ammonia or defaecated as faeces, and this process is repeated throughout the food web. Excreted ammonia is immediately available to be recycled through algae, or oxidised to nitrate by nitrifying bacteria. Faeces add to the pool of organic detritus in sediments and deep layers of the water column which is degraded by bacteria, first to ammonia and then nitrified to nitrate. In general, ammonia is taken up by micro- and pico-planktonic algae, and nitrate by the larger algae in the water column, such as diatoms. The transfer of energy from micro-algae up the food web involves more trophic steps, and is therefore less efficient, than for the larger algae, so ammonia assimilation contributes rather less to higher trophic level production than nitrate assimilation.

Denitrification and anammox are the major processes that remove nitrogen from the ecosystem and have the potential to counterbalance nitrogen inputs. Denitrification involves the utilisation of nitrate as a source of oxygen by bacteria in the oxidation of organic matter, resulting in release of nitrogen gas. Anammox (anaerobic ammonium oxidation with nitrite) consumes ammonia and has recently been shown to contribute 20-60% of total N_2 production in some continental shelf sediments. However, anammox was found to be insignificant relative to denitrification in a eutrophic coastal sediment (Thamdrup and Dalsgaard, 2002). Anammox has also been observed in the water column of anoxic basins, where it can account for 19–35% of total N_2 formation (Dalsgaard *et al*., 2003; Kuypers *et al*., 2003). Experiments with temperate shelf sediment suggest that the temperature optimum of anammox is lower than that of denitrification (Thamdrup and Dalsgaard, 2002), implying that rising temperature might increase the dominance of denitrification over anammox. However, the effect of temperature on the combined rates of denitrification and anammox are uncertain. Some microbiological studies and a model suggest increased temperatures may decrease denitrification (Kelly-Gerreyn *et al*., 2001).

The biogeochemistry of phosphorus is markedly different from nitrogen. To begin with, there are no processes equivalent to denitrification or anammox which apply to phosphorus since the reduced and free states of the element are unstable in the natural environment. The oxygen present as phosphate is therefore not available to the microbial community to support respiration. The key processes affecting phosphorus dynamics are in the sediments and involve the binding of phosphate to particulate matter, which has a major effect on the distribution between dissolved and particulate phase. Binding causes sediments to act as a sink for phosphate under anoxic conditions, which can subsequently be released as a result of oxygenation (Delaney, 1998; Foy and Lennox, 2006; Mort *et al.,* 2010).

The biogeochemistry of silicate is simpler than for nitrogen or phosphorus. The only significant biological uptake of silicate is by diatoms, which require silicon to produce their rigid frustules. The only mechanism for recycling silicon is the dissolution of biogenic silica from diatom frustules deposited to the seabed with herbivore faeces or by the settlement of algal bloom material. Biogenic silicate dissolution results in the build up of dissolved silicate in sediment pore waters and a net flux to the water column. However, diagenetic process in some sediments can cause the deposition of authigenic minerals acting as a sink for silicon (Mackin and Aller, 1989; Chou and Wollast, 1997).

Due to the specific requirement of diatoms for silicate and their role in the ecosystem as a vector for the flux of nitrate-nitrogen through the food web, changes in the nitrogen:silicon and phosphoris:silicon ratios of freshwater discharges to the sea have the potential to cause significant changes to the marine system. Modification of phytoplankton species composition due to nutrient ratios has been reported for the

Baltic and Black Seas (Humborg *et al*., 2000), and other aquatic environments (Conley *et al*., 1993).

1. What is already happening?

High frequency (~weekly), long-term (>10 years duration) monitoring data sets from fixed point locations have proved useful in documenting changes in nutrient concentrations, but rather inconclusive regarding the causes of change. Data collected at the Liverpool University's Isle of Man site known as "Cypris" indicate the effect of increased river concentrations on an offshore station. The data show that concentrations increased from the 1950s into the 1970s and then stabilised (Gowen *et al.,* 2002). However, work following the assembly of data by the EU-FP-NOWESP project (Laane *et al.,* 1996a) failed to find links between monitoring sites in the Irish Sea, English Channel and North Sea. Similar trends could be detected at English Channel and North Sea sites but conditions at the Cypris site were the product of different drivers (Laane *et al*., 1996b).

Winter nutrient concentrations are one of the OSPAR suite of eutrophication status indicators, but assessing trends in the CP2 areas is difficult because of the large variability within each region, dependent partly on salinity and sampling location, and also because data collection has been very patchy in space and time. Heath and Beare (2008) summarised as much as possible of the nitrate data from NW European shelf waters collected between 1960 and 2003 by means of a statistical smoothing technique (General Additive Model, GAM). The technique resulted in a regularly gridded, monthly resolution data set, but smoothed both the spatial and temporal variability. The results are therefore a useful summary at the large scale (e.g. whole North Sea), but difficult to interpret at the small scale (e.g. an individual CP2 area), The nitrate data collected during January-March in each CP2 region illustrate the problem (Figure 1). The observations are highly variable, and statistically significant trends over the 45 year period (increasing) are present only in CP2 regions 4 and 5. In CP2 area 5 (Irish Sea and Clyde) in particular, winter nitrate appears to have increased between 1960 and 1990, and then probably stabilised. Fitting a statistical smoother (local regression smoother (Loess; Cleveland *et al*., 1992) to the data suggests fluctuations in all areas during the period but these are not easily related to NW European shelf-wide trends in either freshwater input from rivers (Figure 2), or nitrate inputs from rivers and the atmosphere (Figure 3), or input of Atlantic ocean water to the shelf, e.g. across the northern boundary of the North Sea (Figure 4).

Due to the complexities described above, advances in the understanding of the causes of changes in nutrient concentrations are most likely to result from a combination of simulation modelling and statistical analysis of observations, than from monitoring alone. There are numerous examples of simulation models which have been developed to simulate the consequences of nutrient input to the North Sea (Cugier *et al*., 2005b; Lenhart *et al*., 1997; Patsch and Kuhn, 2008; Patsch and Radach, 1997; Skogen *et al*., 2004; Skogen and Mathisen, 2009). However, few of these make a detailed examination of nutrient inputs from any but the major UK rivers discharging to the North Sea, and few extend to the waters west of the UK.

To address the issues of nutrient inputs to waters around the UK, Heath *et al* . (2002) ran the spatially resolved ERSEM ecosystem model for the European Shelf and compared simulated water quality indicators for contrasting years of marine and terrestrial weather conditions. The indicators were based on OSPAR eutrophication criteria: winter concentrations of dissolved inorganic phosphorus and nitrogen, summer and weekly maximum chlorophyll, annual and weekly maximum primary production, and the annual ratio of diatom to dinoflagellate abundance. The contrasting years were selected on the basis of hydrological, atmospheric and simulated ocean circulation data. 1990 was selected as an extreme year in terms of strong ocean currents and having a UK rainfall distribution biased towards the west. In contrast, 1984 was identified as an opposite extreme, having weak ocean transport and a UK rainfall bias towards the east (Figure 5). Model-wide, river nitrogen and phosphorus inputs in 1984 were 1.4-times those in 1990, but sub-regionally the ratio varied from 0.6 to 2.1 (Figure 6). However, there was no relationship between 1984:1990 ratios of sub-regional water quality indicators and local nutrient inputs. Nevertheless, water quality indicators were overall 10% higher (i.e. less good eutrophication status) in 1984 compared to 1990 (Figure 7), corresponding to the model-wide direction of change in nutrient inputs, but this was also related to the weaker flushing of the shelf waters by Atlantic inflow in 1984.

2. What could happen in the future?

UKCP09 Future Climate projections for low, medium and high emission scenarios indicate a high probability of drier summers and wetter winters in the UK, with the percentage increase in winter rainfall being greatest in the north-west. Only small (<10%) changes in annual rainfall are predicted over the entire UK. However, other predictions of ocean transport indicate the likelihood of intensification in the inflow of Atlantic water onto the European shelf. Hence, combined with the trend of decreasing anthropogenic discharges since the 1980's which is expected to continue due to more stringent legislation, the short to medium term future NW Europe-wide water quality status is likely to be dominated by inter-annual variability and trends in anthropogenic discharges, as has been the case over the past 30 years. However, over 20-50 years it is possible that the smoothed pattern of water quality will begin to look more like the 1990 simulations of Heath *et al*. (2002) than the 1984 simulations, i.e. an underlying improvement in eutrophication conditions driven by rainfall and ocean circulation changes.

North-East Atlantic Summary

Listed below are regional specificities in nutrient enrichment state and possible climate change responses, based on the Charting Progress 2 regions.

Northern North Sea (Region 1)

Region 1 receives runoff (precipitation–evaporation and transpiration) of approximately 1000mm/year from the UK land catchment area. These waters contain relatively low concentrations of nitrogen and phosphorus, but high concentrations of silicate due the catchment geology (Figure 5). The UK nutrient loads (mass per year) to this area are therefore moderate for nitrogen and phosphorus compared to their CP2 regions, but high for silicate (Figure 6). Atmospheric deposition of nitrate in this region is of similar magnitude to river inputs. Nevertheless, the largest impact on variability in nutrient concentrations in this region is very likely to be from ocean inputs (Patsch and Kuhn, 2008; Vermaat *et al*., 2008). Hence the impact of climate change on the nutrient status of region 1 waters will be principally determined by the processes which may affect concentrations in the upper layers of the ocean, e.g. winter mixing depth.

Southern North Sea (Region 2)

Runoff from the land catchment for Region 2 is the lowest in the UK (<300mm/year, Figure 5), but the concentration of nitrogen and phosphorus in these waters is the highest in the UK, and concentrations of silicate are also high (Figure 5). In addition, region 2 is potentially influenced by river-borne nutrients from the very large continental European rivers flowing into the southern North Sea. Hence, variability in the nutrient status of region 2 waters is strongly driven by precipitation patterns and river runoff. Simulated concentrations respond strongly to weather forcing patterns which may be similar to expected future climate conditions, with improved water quality due to dilution of river nutrient loads in winter runoff, and increased flushing rates.

Eastern Channel (Region 3)

Observations of nutrient concentrations from region 3 are sparse. UK runoff is low, but the concentrations of nitrogen and phosphorus in runoff waters are high (Figure 6). UK inputs of nitrate have been stable or decreasing over time, but the area is strongly influenced by nutrient inputs from the River Seine, which have been steadily increasing with time (Cugier *et al.,* 2005a). Variability in the nutrient status of area 3 is likely to be most strongly influenced by runoff from continental Europe. Current models have difficulty predicting water quality in region 3 due to the bathymetry and the availability of detailed river input data.

Western Channel & Celtic Sea (Region 4)

Runoff to region 4 is similar to region 1 (approximately 1000 mm/year), but concentrations of nitrogen and phosphorus in runoff waters are much higher (Figure 5). Observations of nutrient concentrations in this region are sparse prior to 1997 apart from the time-series sampling at station E1 off Plymouth, but transport of ocean water from across the shelf edge is an important component of oceanographic variability (Laane *et al.,* 1996b). Little is known about the likely consequences of climate change for this process, so predictions of likely climate impacts on nutrient concentrations are very uncertain.

Irish Sea (Region 5)

Region 5 receives large inputs of nutrient from rivers, especially silicon. Simulated nutrient concentrations respond strongly to weather forcing, with conditions which may be similar to future climate predictions resulting in improved water quality. However, the future nutrient state of area 5 is most likely to depend mainly on future trends in anthropogenic inputs.

Minches and western Scotland (Region 6)

Runoff from the catchments discharging into region 6 is the highest in the UK, with values exceeding 2000 mm/year (Figure 5). However, concentrations of nitrogen, phosphorus and silicate in these waters are the lowest of all of the CP2 catchments (Figure 5), and consequently the river nutrient inputs are small, especially for nitrogen and phosphorus (Figure 6). Winter concentrations will be primarily influenced by on-shelf mixing of ocean water and along-shelf transport from the Irish Sea (CP2 region 5). The factors affecting variability in these processes are well understood. Hence, the impact of climate change on nutrient status of area 6 is very uncertain, but not likely to be greatly influenced by precipitation patterns despite the fact that the catchment is forecast to experience the greatest change in winter rainfall. Anthropogenic inputs of nutrient are only a small component of the regional nutrient budget, though at the inshore local scale nutrient inputs from aquaculture are important in some areas.

Scottish Continental Shelf (Region 7)

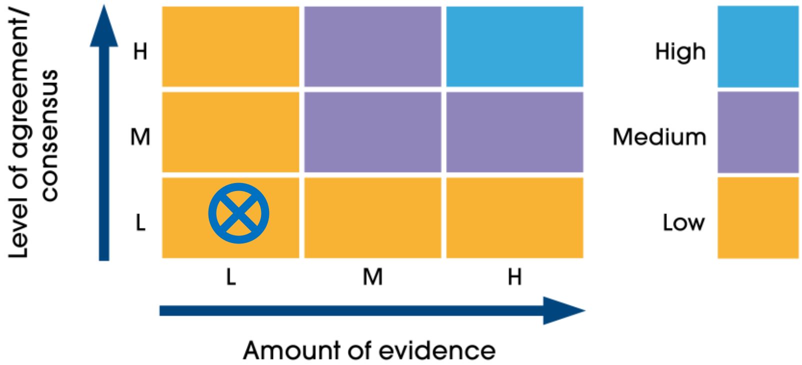
Freshwater inputs, and runoff nutrient concentrations, are small for region 7 and annual inputs of nitrogen and phosphorus are among the lowest in the UK. Winter nitrate concentrations are probably mainly influenced by mixing from the ocean. Simulated nutrient status indicators were relatively insensitive to weather conditions which may represent future climate conditions, though these do not accurately reflect variability in either oceanic nutrient concentrations or the processes affecting exchange across the shelf edge. Hence, the nutrient status of region 7 with respect to climate change is uncertain.

Atlantic Northwest approaches, Rockall Bank and Trough and Faroe-Shetland Channel (Region 8)

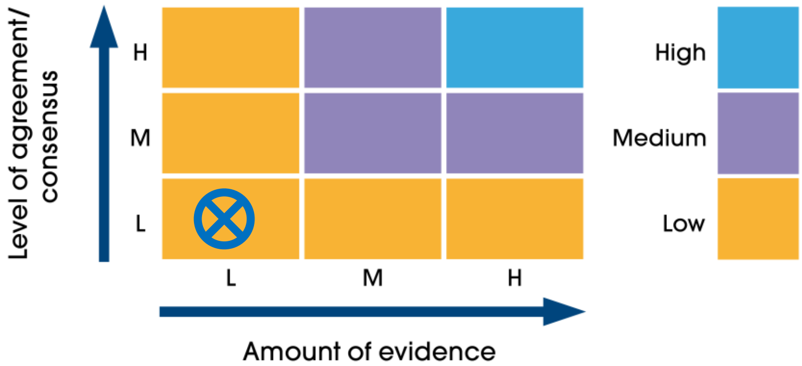
There is little information on which to conduct an assessment of the eutrophication status of this region. However, it receives no land inputs of nutrient, so external inputs are entirely due to atmospheric deposition, upwelling and vertical mixing, and ocean transport. All of these factors may vary with expected patterns of climate change. Hence, we can suggest that the nutrient status of area 8 may be subject to influence by climate change, but that the sensitivity is very uncertain.

3. Confidence in the science

What is already happening: ***Low***



What could happen: ***Low***



We are not really able to say with any confidence whether climate change will lead to an improvement or degradation of nutrient status. Partly this is because in most areas nutrient concentrations are a product of anthropogenic inputs, not natural climate effects.

4. Knowledge gaps

The top priority knowledge gaps that need to be addressed in the short term to provide better advice to be given to policy makers are:

1. Likely changes in river inputs - this research is underway.
2. Better understanding of the role and temperature dependence of denitrification and anammox – the little research on this that has been done highlights large uncertainties (Brion *et al*., 2004; Kelly-Gerreyn *et al*., 2001).
3. Changes in the flow of Atlantic water may be an important control of the North Sea ecosystem (Reid *et al*., 2001) but numerical models that might be used to assess these changes with climate change have only a poor skill level when determining cross-shelf exchange (Huthnance, 1995, 1997).
4. The relative effects of increased storminess and increased stratification have not yet been examined for shelf sea systems.

With respect to river inputs, the current knowledge of nutrient fluxes could be improved by the inclusion of discharge estimates from un-monitored parts of the catchments (which constitute more than 25% in some areas), and ground water seepage. Using catchment models such as applied by Cugier *et al*. (2005b) and Lancelot *et al*. (2007), and with a better understanding of denitrification and anammox, it should then be possible to predict the consequences of changing rainfall and temperature for nutrient discharge to the sea.

Continued collection of time series data is required. This should be done in conjunction with new systems of monitoring using buoys and Ferryboxes. They provide the high resolution data required to deconvolute and quantify the complex set of processes that control nutrient supply and eutrophication by the validation and calibration of numerical models.

5. Socio-economic impacts

Nutrient enrichment beyond normal concentrations may lead to the symptoms of eutrophication which degrade water quality for recreational and fisheries use, and become damaging to benthos, as a result of algal blooms and de-oxygenation. Identification of a water body as eutrophic due to anthropogenic nutrient enrichment results in significant additional costs for water treatment authorities, and for agriculture in relation to measures for the reduction of nutrient leaching.

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ERSEM

The European Regional Seas Ecosystem Model (ERSEM) is a complex plankton functional type (PFT) model developed in the context of the North Sea but now finding wider application (Baretta *et al,* 1995; Blackford *et al*, 2004). The POLCOMS hydrodynamic model is a three dimensional baroclinic circulation model in this case set up for the UK shelf seas, taking boundary conditions from wider area versions of the same model. It is described in detail in Holt and James (2001). The ERSEM-POLCOMS model demonstrates some skill in reproducing regional observations (Holt *et al,* 2005).

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7. Figures

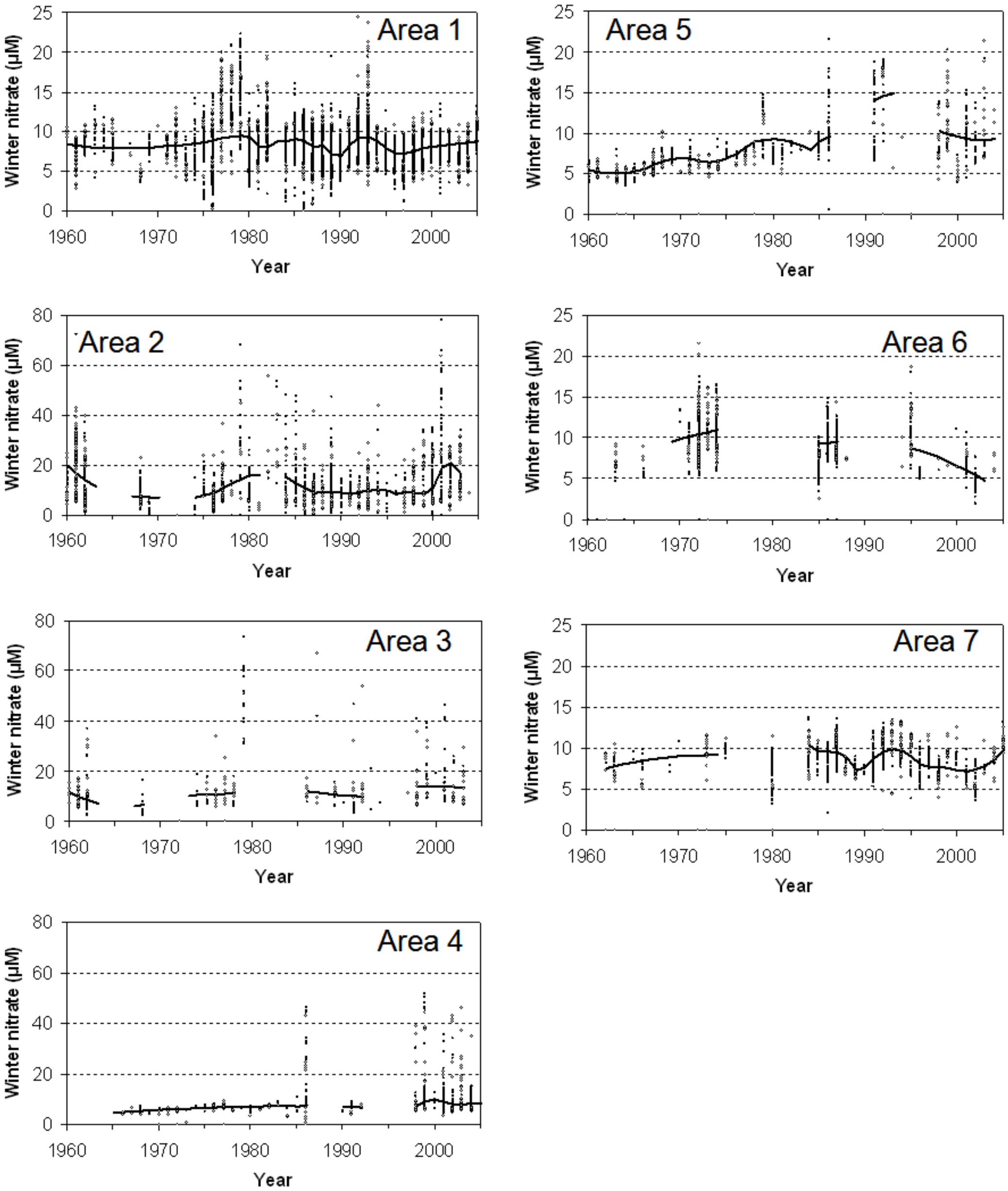

***Figure 1**. Winter nitrate concentrations in each of the CP2 areas between 1960 and 2005. The points are observations within each area collected during January-March from the data compilation of Heath and Beare (2008), The lines are loess smoothers through the observations. Note that the scale-maximum of nitrate varies between areas.*

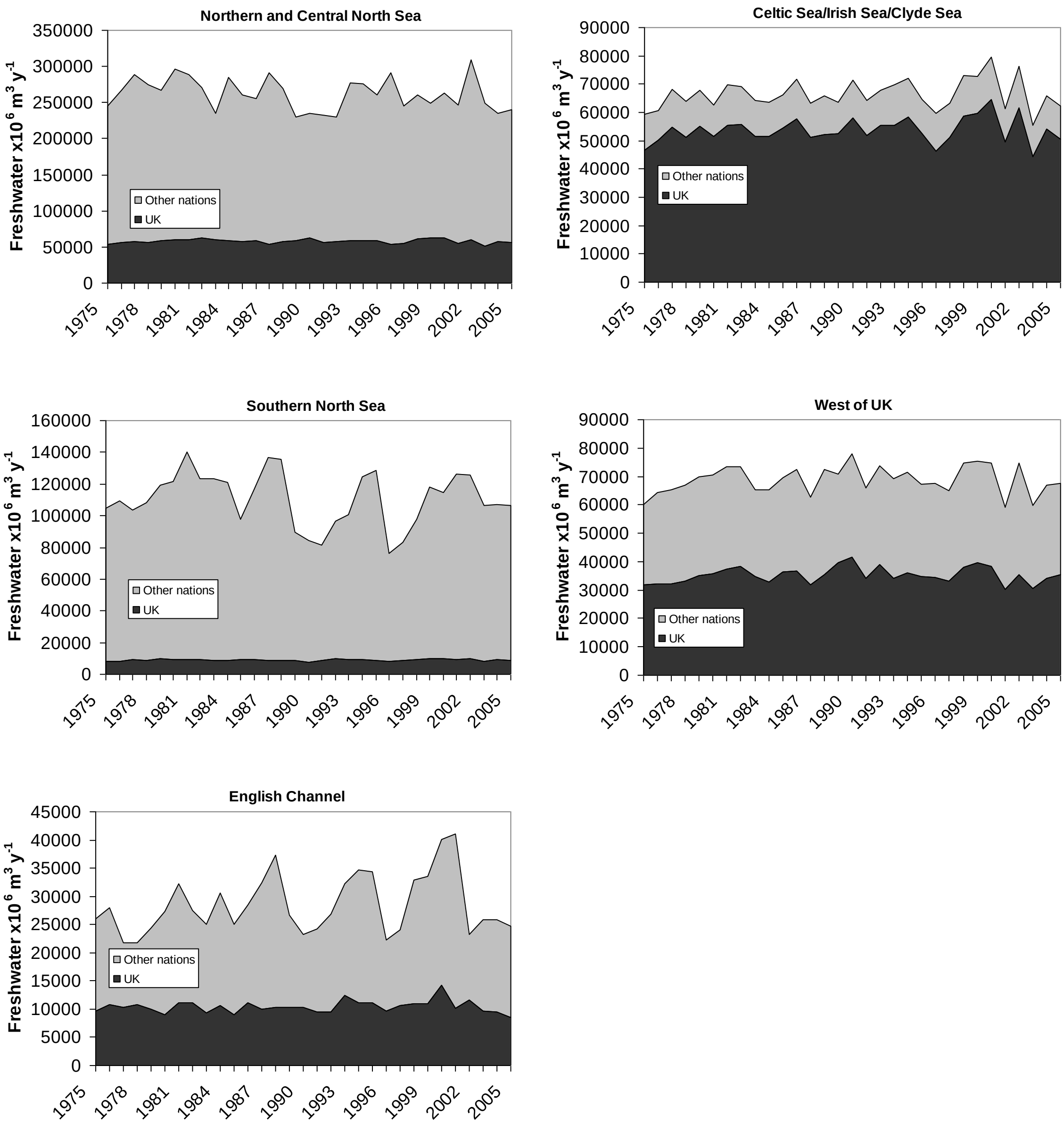

Figure 2. *Annual freshwater inputs from rivers in the UK and other nation states discharging to each of five regions of the NW European shelf during 1975-2005. UK CP2 area 1 and the eastern part of area 7 (east of 4W) are contained within the Northern and Central North Sea region. CP2 area 2 is contained within the Southern North Sea region. CP2 area 3 and the south-eastern part of 4 (east of 6W and south of 50N) are within the English Channel region. CP2 area 5 and the remaining part of area 4 are within the Celtic, Irish and Clyde Sea region. CP2 areas 6 and western part of 7 (west of 5W) are within the West of UK region which also includes the waters west of Ireland. Data from Heath (2007).*

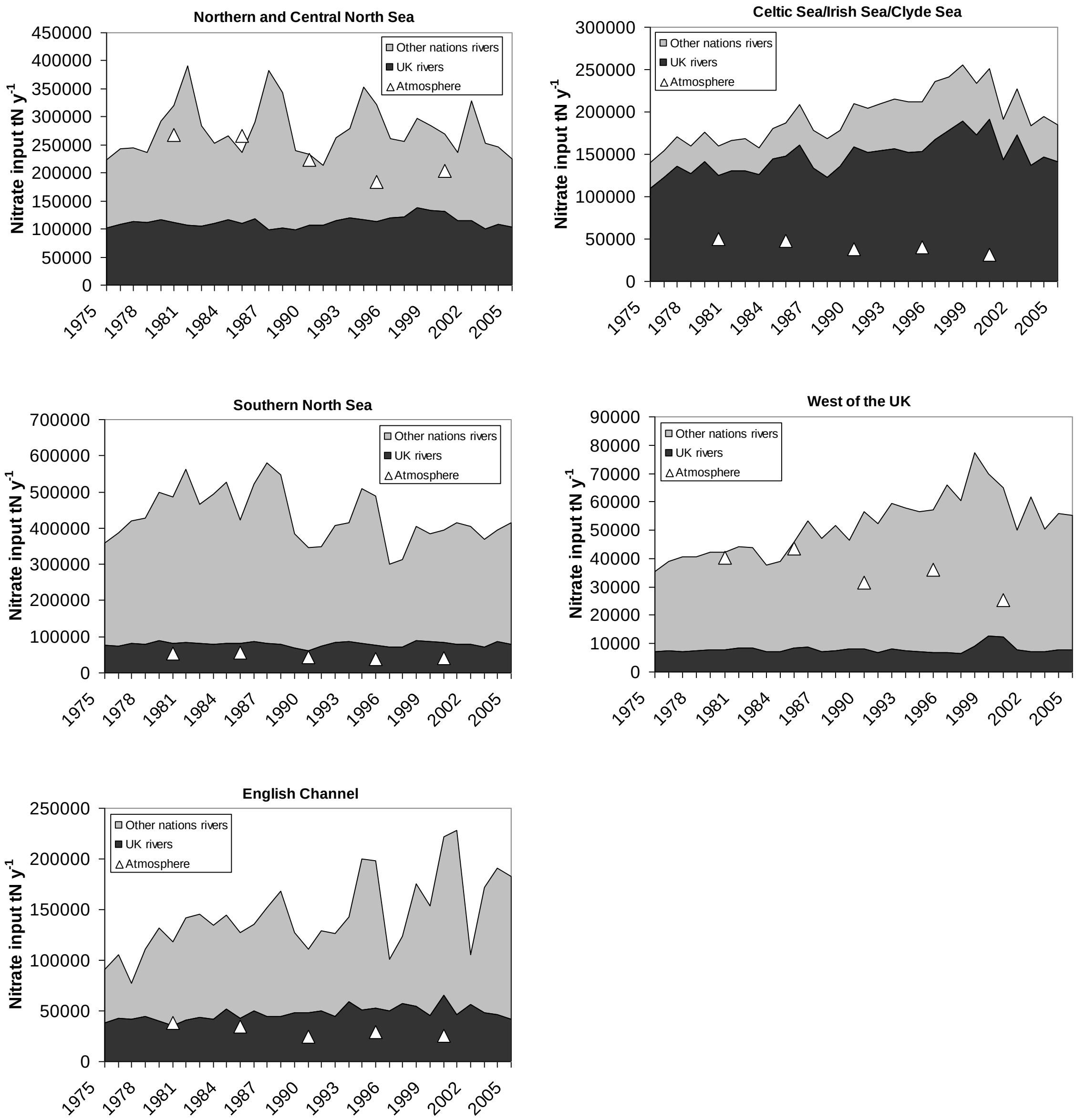

Figure 3. *Shaded areas: Annual nitrate inputs from rivers in the UK and other nation states discharging to each of five regions of the NW European shelf during 1975-2005. Triangle symbols: Annual nitrate inputs from wet and dry atmospheric deposition to the same five regions. UK CP2 area 1 and the eastern part of area 7 (east of 4W) are contained within the Northern and Central North Sea region. CP2 area 2 is contained within the Southern North Sea region. CP2 area 3 and the south-eastern part of 4 (east of 6W and south of 50N) are within the English Channel region. CP2 area 5 and the remaining part of area 4 are within the Celtic, Irish and Clyde Sea region. CP2 areas 6 and western part of 7 (west of 5W) are within the West of UK region which also includes the waters west of Ireland. River data from Heath (2007). Atmospheric data from the EMEP data centre.*

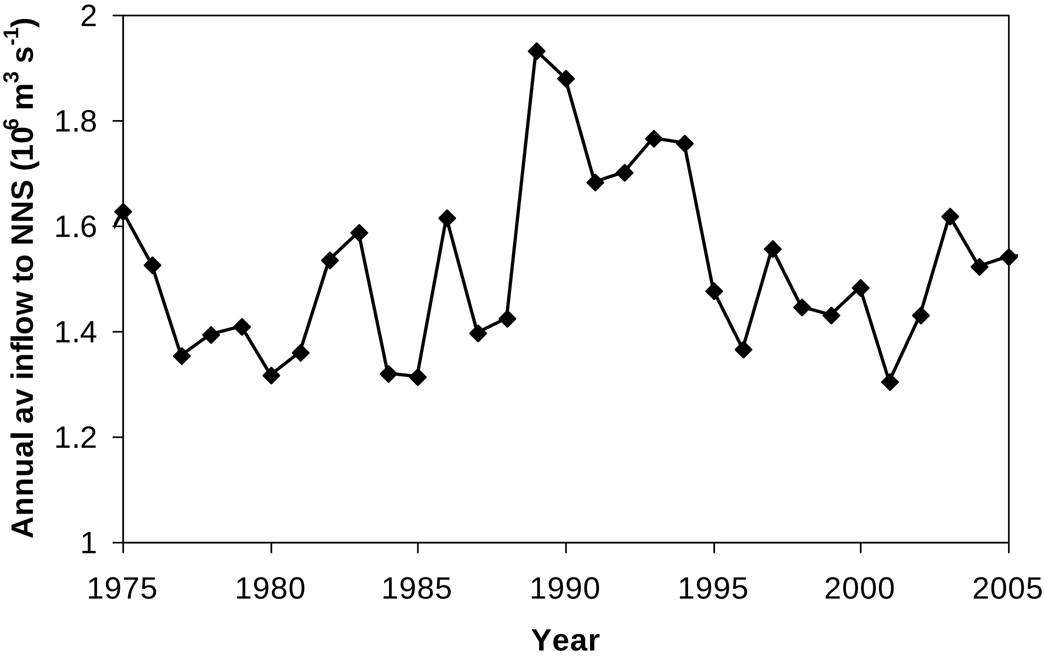

Figure 4. *Annual averaged inflow of ocean water into the Northern North Sea through a transect from the Pentland Firth, through Shetland to Norway. Data from the NORWECOM ocean circulation model (courtesy of Morten Skogen, IMR Norway; Skogen et al 1997, Skogen and Soiland 1998).*

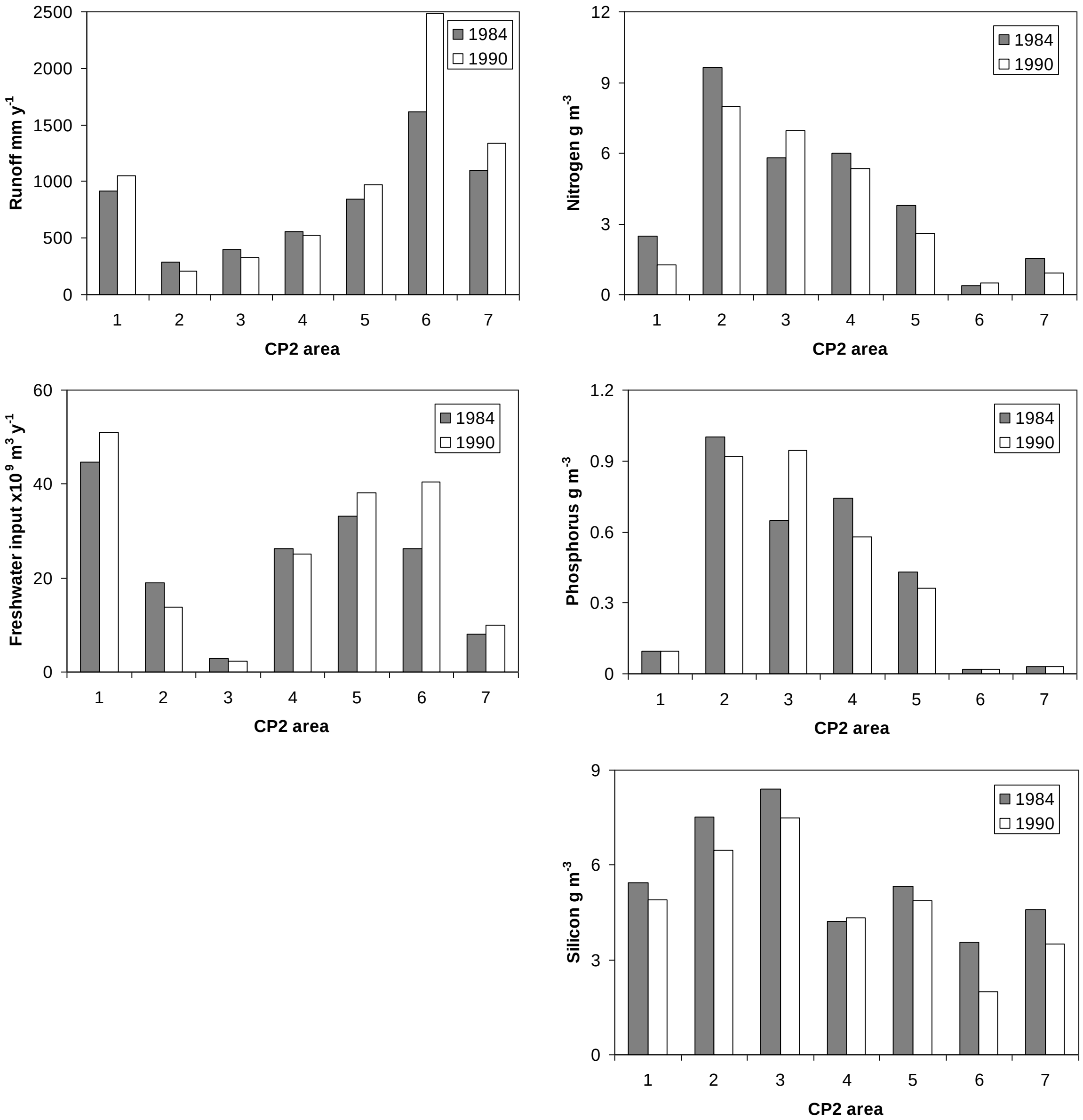

Figure 5. *left column: UK Runoff (mm) and freshwater input (runoff x catchment area) to each CP2 area in 1984 and 1990. Right column: Flow-weighted concentrations of nitrogen, phosphorus and silicon in UK river inputs to each of the CP2 areas in 1984 and 1990. Data from Heath et al. (2002).*

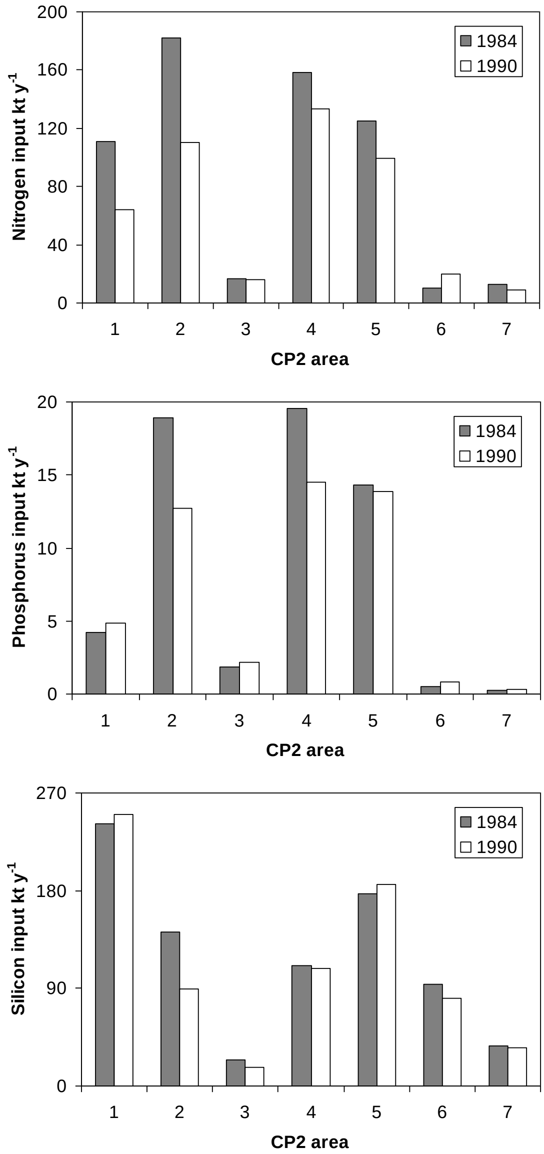

Figure 6. *UK annual inputs of nitrogen, phosphorus and silicon to each of the CP2 areas in 1984 and 1990. Data from Heath et al. (2002).*

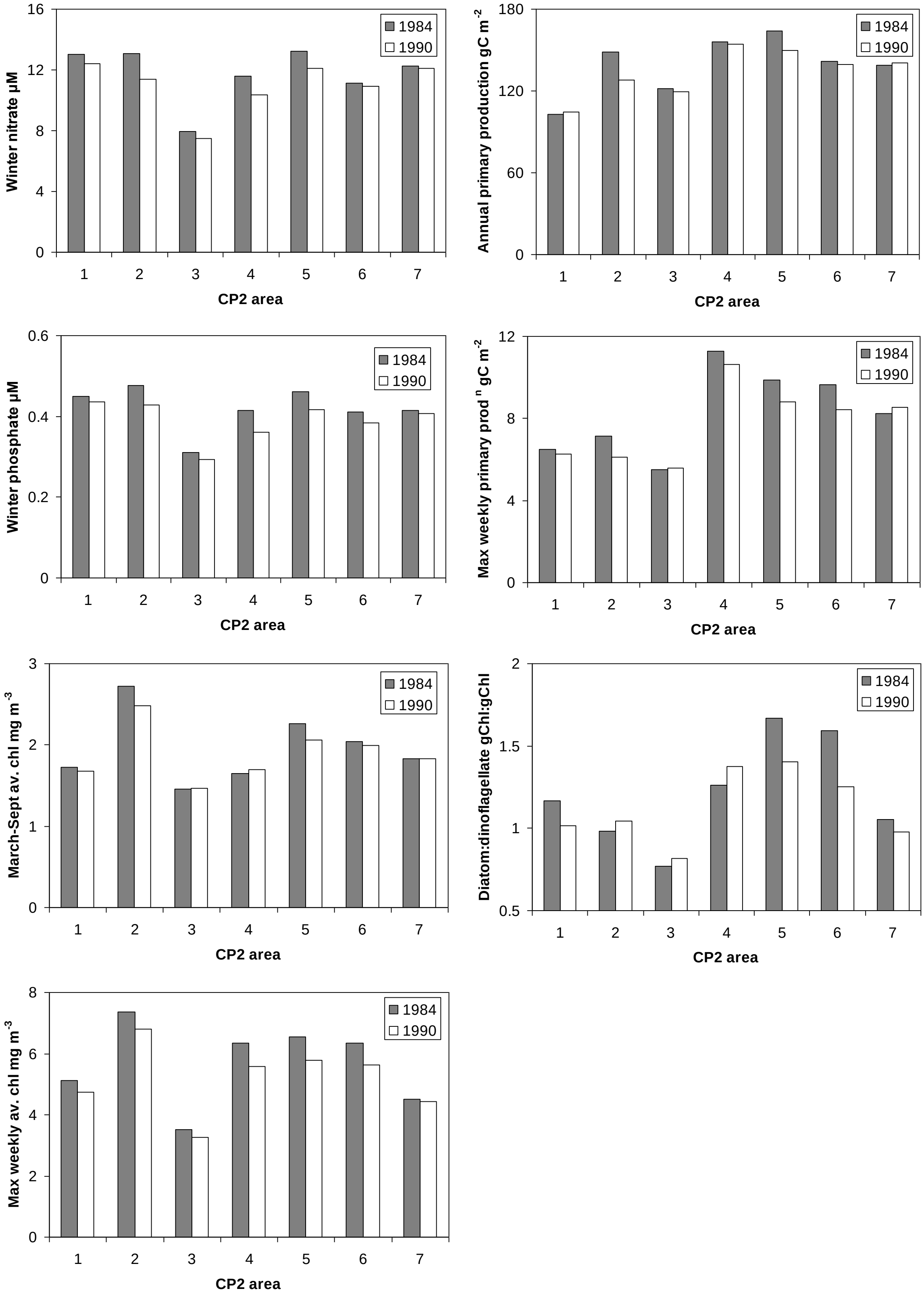

Figure 7. *Simulated OSPAR eutrophication indicators in each of the CP2 areas for 1984 and 1990 derived using ERSEM (Heath et al. 2002). Note that the river input driving data for the model did not include discharges to the English Channel from France, so results for CP2 area 3 should be treated with caution.*