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Assessing Flux Rates from Isotope Dilution Experiments and Numerical Modelling: Results for ^{15}N and ^{135}Ba Tracer Experiments

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Accurate understanding of biogeochemical processes in marine environments requires a critical evaluation of the methods and the models used in data processing. Typically, tracer incorporation experiments used to assess uptake of substrate by phytoplankton are based on the measurement of element, or compound concentrations and on isotopic composition. Generally these results are used in forward models providing flux rates. Often, however, the reverse approach is of interest. One would like to invert directly the measurements in terms of poorly known but critical model parameters or variables such as chemical reaction rates and corresponding isotopic ratios. Of primary importance here are the theories behind error statistics and the evolution of error forecast. A general framework to study the propagation of errors (random and systematic) in models used to compute nitrogen flux rates from ^{15}N tracer experiments was developed via numerical modelling. This approach allowed to compare the estimation behaviour of various model equations with respect to the effect of (i) simultaneous uptake of different nitrogen sources; (ii) nitrogen regeneration; (iii) dissolved organic nitrogen release and (iv) nitrogen loss during the incubation experiment on substrate concentrations and on isotopic ratios. A similar approach was applied to ^{135}Ba tracer experiments to assess for instance the effect of different modes of Ba incorporation (active uptake versus adsorption). This analysis proved that the accuracy of estimated flux rates and to some extent their precision were rather poor, sometimes to the point of making results meaningless. The magnitude of the bias is of course dependent on the assumptions and constraints underlying each model, but too often the "true" or reference values fell outside the calculated limits of confidence. To overcome this situation, the differential equations, corresponding to the numerical approach, were re-formulated and integrated, providing a system of implicit non-linear equations that can be solved for flux rates using recursive methods. The constrained least squares method and the handling of errors is illustrated with numerical examples based on experimental data obtained in the framework of Southern Ocean expeditions (SAZ '98 and ANTARES-4).