



## **PROXIES AND NUMERICAL TOOLS FOR ASSESSING ORGANIC CARBON EXPORT FLUX AND DEEP OCEAN PROCESSING**

GOA-I (2001 – 2006) Summary

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## **1. What we learned from GOA I (2001-2006)**

The subject of GOA I was to contribute to a better understanding of the functioning of the biological carbon pump and of the reprocessing of organic carbon in the subsurface ocean. More specifically, the objectives of the research project were set out to address the following questions:

- What are the relationships between new and export productions?
- How does the carbon flux, determined using the  $^{15}\text{N}$  isotope techniques and the Ba proxy, relate to export production?
- What are the advantages, problems, uncertainties (and their magnitudes) on the above methods?
- If they differ, what are the main causes of discrepancy and how can they be resolved?

In pursuit of its goal, GOA I was structured around four research themes, each addressing a number of specific issues. The strategy applied relied on the use of different, proxies of carbon processing, rather than focussing directly on carbon itself. Well selected proxies can be particularly useful since they are more sensitive than the target process or element itself. A drawback, however, often resides in converting the proxy information into accurate carbon terms.

Underway we implemented one further method for assessing carbon export, namely the  $^{234}\text{Th}$  deficit method, and compared its outcome with those obtained via the other proxies mentioned above.

An overview of the ANCH publications related to these key issues is available in section 8.1. The main outcomes to date are the following:

### **1.1. Theme 1: Compilation of existing data and data acquisition**

We have collected and are still collecting information such as relevant literature on the GOA theme. This bibliography, as well as other GOA materials, data and individual publications can be found on our Web site at <http://homepages.vub.ac.be/~adebrauw/GOA/>.

We first elaborated an archiving and extraction system for data from previous programmes and cruises in which the ANCH group participated. The Ocean Margin Exchange project OMEX (Marine Science and Technology EU programme) was an intensive measurement and modelling study of the exchanges of matter and energy across the ocean margin — the interface between the open Atlantic Ocean and the European continental shelf. The OMEX fieldwork was undertaken along the northwest European shelf break (OMEX I 1993 – 1995)

and at the northwest Iberian margin (OMEX II 1997 – 1999). It has a unique database available at <http://www.bodc.ac.uk/projects/european/omex/>.

Subsequently we participated in several Southern Ocean expeditions in the framework of Federal Science Policy programmes SPSP I and II: 1/ the SAZ'98 cruise (Jan-Mar 1998) to the Subantarctic Zone and Polar Front Zone at 142-145°E, south of Tasmania; 2/ the ANTARES 4 cruise (Jan.-Feb. 1999) to the Crozet-Kerguelen Basin; 3/ the CLIVAR-SR3 cruise (Nov-Dec 2001), covering the whole Southern Ocean basin and the major frontal systems between Tasmania and Antarctica. All GOA-relevant publications issuing from these studies are listed in section 8.1.

Furthermore, recently accomplished cruises continue to generate results which are progressively transferred and stored in the GOA database. Between 2001 and 2005, ANCH members participated to the following expeditions:

- EIFEX (Jan – Mar 2004): (<http://www.awi-bremerhaven.de/AWI/Presse/PM/pm04-1.hj/040402EIFEX-e.html>). The large-scale experiment EIFEX (European Iron Fertilisation Experiment) was conducted in the Antarctic Circumpolar Current to find out the effect of Fe fertilization on the fate of organic matter produced by algae. More specifically, the objective was to find out whether plankton material is converted back into the greenhouse gas carbon dioxide in the surface layer or whether a substantial portion sinks out to the deep ocean which would mean long-term removal of carbon dioxide from the atmosphere.
- VERTIGO I Station ALOHA, Hawaii (Jun-Jul 2004). (<http://www.whoi.edu/science/MCG/cafethorium/website/cruises/vertigo.html>). The investigation area, north of the island of Oahu is the location of the U.S. Hawaii Ocean Time-series (HOT) program, which has been operating for the past 16 years. The focus was on physical and biogeochemical processes affecting carbon export from the mixed layer and its mineralization in the mesopelagic (also called twilight) zone.
- KEOPS (Jan – Feb 2005): ([http://www.obs-vlfr.fr/proof/vt/op/ec/keops/keo\\_obj.htm](http://www.obs-vlfr.fr/proof/vt/op/ec/keops/keo_obj.htm) and <http://www.insu.cnrs.fr/web/article/art.php?art=1325>). The general objective of KEOPS was to better understand the response of the Southern Ocean to the global climate change. Particularly, KEOPS studied the effect of natural iron fertilisation of the ocean by the Kerguelen plateau on the biological pump of CO<sub>2</sub> and on the cycles of other chemical compounds relevant for climate.
- VERTIGO II Northeast Pacific Station "K2" area (Jul-Aug 2005). ([http://www.whoi.edu/science/MCG/cafethorium/website/cruises/vertigo\\_K2overview.html](http://www.whoi.edu/science/MCG/cafethorium/website/cruises/vertigo_K2overview.html)). The investigation area was in the cold and nutrient rich waters of the NW Pacific, a region where particle fluxes out of the surface ocean are thought to be among the

World's highest. A site called "K2" has been chosen for the second VERTIGO research expedition, since this is where the Japanese already maintain deep ocean sediment traps which capture sinking particles below the twilight zone. At "K2" the High Latitude Time Series (HILATS) Observatory program has been in place since 2001. As for VERTIGO I, focus was on physical and biogeochemical processes affecting carbon export from the mixed layer and its mineralization in the twilight zone.

## **1.2. Theme 2: Uncertainty and variability in new production as assessed with 15N incubation experiments**

The concept of new production is one of the cornerstones of biogeochemistry since it constrains both the sustainable exploitation of marine resources and the role of the oceans in the regulation of excess anthropogenic CO<sub>2</sub> accumulation in the atmosphere. New production is merely defined as the portion of primary production driven by externally supplied nutrients. The resulting ratio of new to total primary production is called the *f* ratio. The determination of 15N nitrogen uptake enables the separation of new from regenerated production – i.e. of primary production sustained by nitrate and N<sub>2</sub> from that sustained by regenerated N-nutrients such as ammonium and amino acids (Dugdale and Goering 1967). Assuming a steady state nutrient budget for the upper ocean and an absence of nitrate regeneration in the euphotic zone, Eppley and Peterson (1979) have linked new production to export production via the use of *f* ratio. Although the concept of *f* ratio is simple, its estimation can be rather complicated and has been controversial (Bronk et al., 1994). Hence new production should be considered as “exportable production” rather than “export production” (Sambrotto and Mace, 2000)

We have improved models and protocols to get more reliable data on new production rates. Our work started with a framework to classify types of uncertainty and variability in assessing new production. Uncertainty is divided in parameter uncertainty, model uncertainty and uncertainty due to choice of a given parameterization. Variability covers changing environmental conditions, i.e. eutrophic *versus* oligotrophic (spatial variability), or steady state *versus* non steady state (temporal variability) conditions. In other words, variability is due to differences in properties between different ecosystems.

Regarding modelling, substantial effort has been spent on: (1) parameter optimization (N uptake and remineralisation rates), (2) model accuracy (agreement between modelled data and observations), (3) model precision (random error propagation through calculations) and (4) model selection (selection of relevant parameters/processes in models of different complexity and choices of parameterization). We investigated the reliability of six increasingly complex models, for estimating flux rates between phytoplankton and dissolved N pools in aquatic ecosystems. The development of these models over the last 40 years

reflects increasing realism in the pool and fluxes that constitute the N cycle. Our results show that the likelihood of model failures or biases depends on specific underlying assumptions, but generally increases with duration of the  $^{15}\text{N}$  isotope dilution incubation experiments designed to assess N-uptake and release. Decreasing the exposure times is not necessarily the answer because of experimental uncertainties. In short incubation periods the impact of random errors may become overwhelming, especially when the calculation involves a difference. It follows that for a number of models, properties such as accuracy and precision cannot both be optimized under the same conditions, and a compromise must be struck. Nevertheless, these model comparisons do not solve the problem of statistical inference as they do not yield information on the reliability of the solutions. Oversimplified models risk bias when their underlying assumptions are violated, but overly complex models can misinterpret part of the random noise as relevant processes. Therefore, none of the  $^{15}\text{N}$  model solutions can a priori be rejected, but each should carefully be assessed with hypothesis testing. To address this issue, we developed a generic modelling approach based on mass balance differential equations. This approach is well known in chemical engineering and used the so called compartmental analysis. The model structure is categorized as stochastic and any variables in the model can be expressed by a probability distribution (Elskens et al., 2005). Model parameters are then estimated with a weighted least squares technique (de Brauwere et al. 2005a). A model selection strategy based on a statistical interpretation of the cost function (sum of the weighted least squares residual) was subsequently implemented in order to provide optimal solution subsets corresponding to a given data set. It is noted that the procedure improves the accuracy of the parameter values, making them less sensitive to outlying observations and delivers more reliable final model results (de Brauwere et al., 2005b).

When experimental data are used in calculations (e.g. calculation of uptake and remineralisation rates), the experimental uncertainties are transmitted to a greater or lesser extent into the calculated values. With help of Monte Carlo simulations, we investigated how random errors in a particular measured variable can be magnified or suppressed during model calculations. More specifically, we focused on the following questions: how should a reasonable average be calculated for censored samples (data below detection), and what would be a meaningful measure of the associated uncertainty? The influence of censored data was addressed by means of scenario analysis and case studies. In oligotrophic conditions, such as encountered at the ALOHA station off Hawaii, when nutrient concentrations are below the limit of detection (DL),  $^{15}\text{N}$  tracer additions can dramatically exceed the ambient level and the abundance of the tracer cannot univocally be determined. There are robust statistical procedures that can assign numerical value for the mean and standard deviation of censored data (Berthouex and Brown, 1994). Obviously, because the

measurement error is large relative to the DL value itself, propagation of such uncertainties in the calculations yields a coefficient of variation on the N flux rate that is extremely high (50 to 100%). On the contrary when the nutrient concentrations are well above detection (under repeatability conditions), the coefficient of variation on the model calculations may be less than 5%. *Unreliable estimates of ambient substrate concentrations can, therefore, be considered as one of the most serious drawbacks to our present interpretation of the 15N tracer data.*

New production is calculated as the product of  $f$  ratio (15N tracer data) with total primary production (PP, 13C tracer data). For expressions involving a simple multiplication, the overall uncertainty is directly proportional to the square of the relative standard deviations of each variable entering into the calculation. Accordingly, the relative uncertainty in the final result is not much larger than the largest relative uncertainty used to calculate it, namely the uncertainty on the 15N tracer data. Yet it was found that experimental uncertainty was not necessarily the most important source of variation on the new production assessment. For example in a series of tracer experiments conducted over a 3 week period in the NW Pacific (VERTIGO II), the most important source of variation on new production was the temporal variability in the phytoplankton productivity (about 50%) whilst the uncertainty on each replicate measurement were below 10% (Elskens et al., Ocean Sciences Meeting 2006).

To summarize, substantial effort was spent on improving current methods for new production assessment and developing procedures to deal with uncertainty and variability. In general, uncertainty can be reduced by gathering additional information (better data, better models), whereas variability will not change as a result of better or more extensive measurements. Various improvements for further research are given in section 3. These include the (1) determination of 13C-DOC release rates during incubation in order to separate new production into dissolved and particulate fluxes, (2) the combined use of 13C, 15N and 30Si to provide an estimate of total primary production, new production and diatom-sustained production within a single incubation experiment (3) the use of inverse modelling to provide primary production and new production estimates at the ocean basin scale, and (4) the adaptation of 15N models for scenario analyses.

### **1.3. Theme 3: Comparison of new and export production**

Comparison of new and export production was achieved in functionally contrasting ocean settings including the European continental/ocean margin in the North Atlantic, (OMEX phase I), the Southern Ocean (CLIVAR-SR3) and the Pacific Ocean (VERTIGO I and II).

During OMEX phase I, the estimation of new production with 15N tracer data is equivalent to  $\sim 82 \text{ g C m}^{-2} \text{ y}^{-1}$ , which is half of the estimated annual primary production. This is

consistent with the estimated obtained by comparing the grazing pressure with primary production, indicating that 16 to 60% of the primary production is not used by heterotrophs in the surface mixed layer (Joint et al., 2001). For the period April to September, we also estimated new production using remote sensing images and an algorithm relating  $f$  ratio to the nitrate concentrations (Elskens et al., 1999). The satellite based estimate of new production is  $46 \text{ g C m}^{-2}$ , which compares reasonably with the  $57 \text{ g C m}^{-2}$  estimated for the same period (April through September) using  $^{15}\text{N}$  as a tracer. This gives credence to the estimated new production obtained from satellite remote sensing and its use to investigate the spatial variability in  $f$  ratio. During the spring bloom, satellite data suggests that the region of cool water along the shelf break translates into area of elevated  $f$  ratio ( $> 0.5$ , Elskens et al. 1999). From June to winter, new production is low and ammonium the most important nitrogen source for the phytoplankton. This is consistent with the higher heterotrophic activity in this period since with net heterotrophy, ammonium production should be maximised (Joint et al., 2001). The change in nutrient concentration was also used to quantify the potential importance of diatoms in the spring bloom. Winter concentrations of nitrate and silicate were  $8.7 \mu\text{M}$  and  $2.8 \mu\text{M}$ , respectively (Hyde et al., 2001). Assuming that diatoms utilise nitrate and silicate with an atomic ratio of 1, that silicates was depleted in the spring bloom and that silicate was not rapidly recycled, diatoms would account for about 32% of the new production in April and May (Joint et al., 2001).

Finally, how does the material collected in the sediment traps compare with the yearly estimates of new production? Material from the sediment traps was analysed for Ba barite and the data were used to calculate carbon export flux according to the rationale of François et al. (1995). Using the excess Ba fluxes corrected for trapping efficiency and advection (Antia et al., 2001) as well as for the fact that in continental margin settings a smaller amount of Ba-barite is produced per unit particulate organic carbon (POC) exported as compared to open ocean systems, our data suggest particulate carbon export in the OMEX slope region to be of the order  $8 \text{ to } 18 \text{ g C m}^{-2} \text{ y}^{-1}$  (Dehairs et al., 2000). Such values are lower by a factor 3 to 6 than estimates of new production based on the  $^{15}\text{N}$  data ( $80 \text{ g C m}^{-2} \text{ y}^{-1}$ ) and suggest that not all of the exportable carbon estimated from new production is exported as a vertical POC flux; part may be exported out of the area by advective transport of either POC and DOC. As a matter of fact both approaches would converge, if a significant fraction of new production ends up as dissolved organic matter (DOM) instead of particulate organic matter (POM). A simulation study has suggested that between 20 to 40% of the total organic matter production should be released as net fluxes of DOM to support the Ba approach (Elskens, 1999). These values were not confirmed because of experimental drawbacks in assessing DOM release rates, but seem compatible with literature information (Bronk et al., 1994). The development of a new automated setup for stable isotope analysis

of dissolved organic carbon (Bouillon et al., 2006) will clearly help us to better appreciate this problem in further field works (see also section 3)

During CLIVAR-SR3 in spring 2001, the Antarctic Zone South (AZ-S) and the Seasonal Ice Zone (SIZ) constituted the region of highest new production (up to 240 mg C m<sup>-2</sup> d<sup>-1</sup>) while new production in the SubAntarctic Zone (SAZ), the Polar Front Zone (PFZ) and the Inter Polar Front Zone (IPFZ), values reached only about 70 mg C m<sup>-2</sup> d<sup>-1</sup>, with SAZ values slightly exceeding those for PFZ-IPZ. The AZ-S and SIZ had highest f-ratios, reaching up to 0.61. Lowest f-ratios were observed in the SAZ (0.38) and intermediate values (0.56) in the PFZ. The latitudinal trend of new production during spring 2001 along 145°E is similar to the one for the <sup>234</sup>Th flux obtained for the same cruise.

Deficit of <sup>234</sup>Th activity (relative to its parent <sup>238</sup>U) in the upper mixed layer is indicative of particle export. Knowledge of POC/<sup>234</sup>Th ratios of settling particles gives access to the POC export flux. During spring 2001 (CLIVAR-SR3) <sup>234</sup>Th fluxes along 145°E were low in the north (ca. 630 dpm m<sup>-2</sup> d<sup>-1</sup>), minimal in the Polar and Inter Polar Front Zones (ca. 300 dpm m<sup>-2</sup> d<sup>-1</sup>) and high in the south (ca. 3000 dpm m<sup>-2</sup> d<sup>-1</sup>). <sup>234</sup>Th export fluxes were converted into particulate organic carbon (POC) flux by multiplying with the POC/<sup>234</sup>Th ratio of large particles (55-210µm), assumed to represent the sinking particles. During the CLIVAR-SR3 cruise export production ranged from 20 mg C m<sup>-2</sup> d<sup>-1</sup> in the PFZ to 670 mg C m<sup>-2</sup> d<sup>-1</sup> in the SIZ at 64°S. Our results indicate low particle export in the SAZ and SAF, very low particle export in the PFZ and IPFZ and high export in the AZ-S and SIZ during spring 2001. This latitudinal trend is in quite good agreement with new production data for the same cruise. The very low export production and new production in the PFZ and IPFZ contrast with the widely accepted idea that the Polar Front enhances primary and export production. This could be specific to the Australian sector because of local hydrodynamic conditions associated with a double front structure.

Iron and ammonium concentrations may strongly affect the relative importance of exportable production vs. total production (i.e. the f-ratio). In addition to their individual effects, the combined effect of ammonium and iron on f-ratio was investigated during spring 2001 (CLIVAR-SR3, 145°E). In the HNLC areas of the SAZ, PFZ and AZ-S f-ratio is lowered by ammonium addition and enhanced by iron addition. It was observed that enhancement of the f-ratio due to Fe addition depends on the ambient ammonium concentration and it thus appears that the combined effect of ammonium and iron is not simply cumulative. Our results imply that there is no simple relationship between export production and iron availability. Ammonium appears to counter the effects of iron addition on export production, particularly for HNLC areas such as the Southern Ocean.

We also investigated the effect of large scale in-situ iron amendment on carbon export. The EIFEX iron fertilisation experiment (January – February 2004) took place in a meso-scale eddy pinched off from the meandering Polar Front in the Atlantic sector. The experiment ran until the decrease of the export flux in contrast to other iron experiments in the Southern Ocean which were interrupted before significant export occurred. The eddy was fertilized with Fe and monitored for 36 days afterwards. A phytoplankton bloom dominated by diatoms was induced with chlorophyll contents reaching close to  $3 \mu\text{g l}^{-1}$  three weeks after the iron infusion. The  $^{234}\text{Th}$  export fluxes at 100 m first decreased to near zero within the first two weeks after the iron infusion. Subsequently  $^{234}\text{Th}$  fluxes increased, reaching values as high as  $8000 \text{ dpm m}^{-2} \text{ d}^{-1}$  one month after the Fe infusion. Such a  $^{234}\text{Th}$  flux is the highest ever recorded and suggests that the bloom broke up rather fast and sunk massively. During the last four days of the experiment the  $^{234}\text{Th}$  flux decreased again to  $1400 \text{ dpm m}^{-2} \text{ d}^{-1}$ . When integrated over the full period of export (i.e. days 15 to 36), the sinking of the Fe-induced bloom exported 44700 to 88000  $\text{dpm m}^{-2}$  of  $^{234}\text{Th}$ . The evolution of  $^{234}\text{Th}$  export versus time during EIFEX was strikingly similar to the one of mesopelagic Baxs content, a proxy for mesopelagic mineralisation of organic carbon.

During the VERTIGO I and II expeditions (Station ALOHA, Hawaii, June-July 2004 and Station K2, NE Pacific; July-August 2005, respectively), we had the opportunity to compare our new production estimates with the POC flux obtained from neutrally buoyant sediment traps (NBST) at 150 m (K. Buesseler et al., Ocean sciences meeting, 2006). At the Aloha station, the estimates of new production based on  $^{15}\text{N}$  tracer data is equivalent to 18 – 38  $\text{mg C m}^{-2} \text{ d}^{-1}$ , which compare reasonably with the 17 to 21  $\text{mg C m}^{-2} \text{ d}^{-1}$  obtained for the same period with the NBST deployment at 150m. The system was apparently in steady state and the experimental uncertainty of the new production was high because of the extreme oligotrophic conditions encountered over the three week sampling period (see section 1.2). There was a large difference in the magnitude of the export flux between VERTIGO I and II expeditions, with fluxes on sinking particles being much higher at station K2. The POC fluxes obtained with the NBST's at 150m amount to 68  $\text{mg C m}^{-2} \text{ d}^{-1}$  (first week of sampling) and 24  $\text{mg C m}^{-2} \text{ d}^{-1}$  (second week of sampling).

Such values at K2 are 2 to 3 times lower than those obtained for the new production and reaching 150 and 70  $\text{mg C m}^{-2} \text{ d}^{-1}$ , for the first and second week, respectively. While the temporal variability in POC flux is clearly documented by both approaches, it also appears that not all of the exportable carbon estimated from new production is effectively exported as a vertical POC flux. These results corroborate OMEX-I results, discussed earlier, and advocate for a better characterization of DOC release rates when estimating new production.

#### **1.4. Theme 4: The mesopelagic Ba (barite) as tracer of mesopelagic organic matter mineralisation**

We assessed mineralization of exported organic carbon using the barium-barite proxy and the algorithm relating particulate Ba with oxygen consumption obtained earlier for the Southern Ocean (Shopova et al., 1996; Dehairs et al., 1997). Excess, non-lithogenic particulate Ba (Baxs, mainly consisting of barite) is associated with phytoplankton derived particles. In the mesopelagic zone a Baxs maximum is a recurrent feature which develops over the season and reflects the influx and mineralization of plankton detritus sinking from the mixed layer. During the summer (SAZ'98) and spring (CLIVAR-SR3) cruises along Southern Ocean WOCE SR3 line (145°E) we observed significant zonal differences in mesopelagic Baxs contents. Compared to the SubAntarctic Zone (SAZ) mesopelagic Baxs contents during spring 2001 were larger and started to increase at shallower depths south of the Polar Front Zone (PFZ) and the Antarctic Zone (AZ), where diatoms were the dominant component of the phytoplankton community. During summer 1998, when mesopelagic Baxs accumulations were larger, a similar latitudinal trend was observed (Cardinal et al., 2001). In contrast, the deep ocean flux of Baxs sampled by moored sediment traps was larger in the nano-phytoplankton dominated SAZ, than in the diatom dominated PFZ, as was observed also for deep particulate organic carbon fluxes. Overall, the results indicate relatively high particulate carbon export and absence of strong mesopelagic mineralisation (7.5–36% of export production) in the SAZ, but relatively low export and strong mesopelagic mineralisation further south in PFZ to SIZ (20–97% of export production). Mesopelagic carbon remineralisation was higher during summer compared to spring. Our findings are supported by results for the  $^{234}\text{Th}$  and N-uptake proxies obtained for the same cruise.

Overall highest organic carbon export and mineralization in the Southern Ocean (as reflected by mesopelagic excess Ba) were observed in areas characterized by strongly enhanced productivities. These are the Crozet Kerguelen basin studied during the Antares 4 cruise (Jan – Feb 1999) and the Kerguelen plateau studied during the KEOPS cruise (Jan – Feb 2005). In the former area the merging of three frontal structures and associated currents (Agulhas retroflection; Subtropical front; SubAntarctic front) in a narrow zonal band, results in sharp physico-chemical gradient sustaining enhanced biomass resulting in high export. Above the Kerguelen plateau, natural Fe advection into the euphotic layer occurs through remobilisation of bottom sediments (the water column is  $\leq 600\text{m}$  depth) and possibly internal wave induced upwelling and spilling of Fe-enriched deep water over the plateau. These are thought to be responsible for enhanced productivities and associated export as well as deep-sea mineralization of organic carbon.

The artificial iron fertilisation of a mesoscale eddy in the Atlantic Polar Front Zone (EIFEX cruise; Jan – Mar 2004) did result in temporarily enhanced particle export ( $^{234}\text{Th}$ -deficit method) which was paralleled by enhanced mesopelagic excess Ba. The deduced intensity of

organic carbon mineralization was, however, not strikingly different from what we observed elsewhere for the natural Southern Ocean. This could possibly reflect more efficient export of organic carbon to the bathypelagic water column, with less under-way mineralization, but final conclusions still have to be drawn regarding these results.

So, overall the mesopelagic particulate Baxs seems to operate quite well as a proxy of organic matter mineralization in the subsurface, twilight zone. However, till recently, no direct comparison between excess particulate Ba concentrations and productivity of heterotrophic bacteria in mesopelagic waters was attempted. This mainly because bacterial activities below the upper 100m are usually very low and also because of uncertainties concerning effects of hydrostatic pressure relieve during deep sea water sampling and incubations under atmospheric pressure. During the VERTIGO I and II expeditions (Station ALOHA, Hawaii, June-July 2004 and Station K2, NW Pacific; July-August 2005, respectively), focussing specifically on twilight zone processes, we had the opportunity to confront our excess Ba results with bacterial production rates obtained for the upper 1000m of water column (B. van Mooy, K. Casciotti, P. Boyd, pers. communic.). The extreme oligotrophic ALOHA site clearly differentiated from the NE Pacific HNLC site, and a positive correlation became clear between bacterial production and excess particulate Ba in the twilight zone. Furthermore, bacterial carbon utilisation rates assessed from Thymidine incorporation and growth efficiency estimates, proved to be of similar magnitude than carbon demand based on Baxs contents. Results also compare well with decreases in POC fluxes over the 150 to 500m depth region based on Neutrally Buoyant Sediment Trap derived POC fluxes, though particle settling flux patterns may appear complex with possible impact of zooplankton migration (K. Buesseler & D. Steinberg, pers. communic., VERTIGO meeting, Feb. 2006, Hawaii). These results are highly encouraging to launch further efforts for combining different methodologies to assess twilight zone organic matter respiration. As a first step, we propose to extend our proxy-tool box, by also including assessment of bacterial production at those depths in the upper 1000m, sampled for Ba.

A first opportunity for such a tight proxy tool comparison resides in the upcoming SAZ-SENSE expedition to the SubAntarctic and Polar Front Zone, south of Australia and scheduled for January. February. 2007. Besides the now 'classical' tools including new production,  $^{234}\text{Th}$  flux, mesopelagic excess Ba accumulation, we will also systematically assess bacterial production via the thymidine incorporation. We will operate in close collaboration with the "Ecologie des Systèmes Aquatiques" (Université Libre de Bruxelles) team who has long standing experience in assessing bacterial production. Furthermore results will be compared also with direct oxygen consumption measurements from in-situ incubated parcels of seawaters with electrode monitoring of  $\text{O}_2$  evolution and on board

long-term BOD incubations, via Winkler titration (P. Boyd, NIWA, University of Otago, New Zealand).