Long-Term Variability in the Horizontal Exchanges Between the Benthic Boundary Layer Over the Black Sea Shelf and the Deep Sea and its Potential Role in Carbon Sequestration (contribution to S1.6.4 - Long-

term changes in the environmental parameters in the benthic boundary layers on the Black Sea shelves)

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Historical archives from a variety of sources were scanned to identify long-term time series of hydrological and biochemical parameters in the benthic boundary layer on the Western Black Sea shelves and adjacent deep sea regions. These data were processed in order to identify preferable sites and timing for carbon export from the shelves into the Cold Intermediate Layer (CIL) due to horizontal exchanges. Decadal trends, smooth changes and rapid regime shifts in the parameters of the benthic boundary layer which facilitate carbon export from the shelves were assessed at selected locations. Particular emphasis was placed on the last 30 years of the 20th century.

The meta data base was collated using publicly available and grey data sources as well as the data specifically rescued and converted from paper into digital form by the University of Plymouth.

Analysis revealed that amounts of biochemical data, and in particular the data on dissolved organic carbon (DOC), are not sufficient to provide reasonable temporal and spatial coverage for the analysis so that adequate proxies should be used. The data available for the bottom boundary layer (BBL) was particularly sparse, so that adequate proxies were identified and used.

Analysis of the meta data base shows that suitable proxies for the purpose of estimating the tendencies in the horizontal movement of DOC, its export from the shelf and subsequent sequestration in the deep sea are the near-bottom temperature and horizontal temperature contrast below the upper thermocline. The physical reason for this is that interannual /interdecadal variations in the near-bottom temperature are directly related with the intensity and the volume of cold waters (Ivanov *et al.*, 2000) which are formed on the shelf and then exported into the deep sea. The chemical structure of the Black Sea waters is largely determined by the location and the strength of the pycnocline. The oxycline and the chemocline occur at the same depth intervals as the halocline, because of similarity in the mechanisms of vertical exchanges (Ozsoy and Unluata, 1997).

Despite early claims on possible shoaling of the anoxic interface (Murray et al., 1989), the vertical position and structure of the chemocline appear reasonably stable within the last few decades (Tugrul *et al.,* 1992) However, seasonal and interannual

temperature and salinity variations do exist in the upper layer (Ivanov et al., 1997a,b) that are subsequently evidenced in the bottom boundary layer on the Western shelf due to winter convection.

The majority of the available data suitable for the study of the BBL was taken on the extensive North West shelf, which is the focus of the present report. In this study we identified climatically averaged parameters on a dense horizontal grid of 0.25° as well as monthly anomalies (deviations from the climatology) using over 17,000 stations. Water masses and the chemicals contained therein, which are located in the BBL on the shelf below the upper pycnocline are unlikely to surface in the deep sea and are likely to be locked away from near-surface biogeochemical processes. The layer below the upper pycnocline forms a 'communication channel' for nutrients and carbon to be removed from the shelf ecosystem. Location and intra-annual variability of the 'communication channel' has been established. Waters denser than the pycnocline cover the shelf sea bed over an area of between 17,600 km² in January to 67,000 km² in October. Materials originating on the shelf may be removed to the deep sea within the core of the CIL at densities higher than $\sigma_{\theta} = 14.2 \text{ kg m}^{-3}$.

The interannual variability of the efficiency of exchange processes within the 'communication channel' has been identified. Low shelf-deep sea contrast is taken as an indicator for good exchange and high contrast indicates broken communication between the two regions. Cascading of dense water from the shelf while observed in-situ (Shapiro et al., 2004), seems unlikely to be the main process of shelf-deep sea exchange.

The monthly evolution of temperature anomalies in the individual years within shelf and deep sea compartments revealed that thermohaline intrusions may occur even in warmer than average conditions. In several years the temperature contrast flips between winter and spring showing that the communication frequently breaks down after the winter. The CIL is thus seen as having provinces (or regions) that exchange water masses and chemicals in some years, but not in others. The shelf-deep sea temperature contrast shows strong intra-annual and interannual variability in the communication between different shelf and deep sea, suggesting that the CIL is not a single homogenous water mass.