



Fig. 7. Comparison of discussed POC flux representations and global POC flux data from Lutz et al. (2002). Observations shallower than 1.5 km have been divided by 0.4 to account for the potential undertrapping error (open symbols). Observations: \blacksquare/\square : Atlantic Ocean, \blacklozenge/\lozenge : Pacific Ocean, \ast/\ast : Indian Ocean, \blacktriangle/\triangle : Greenland Sea. POC flux data has been normalised to regional POC export estimates given in Lutz et al. (2002) - Table 2.

needs to aggregate or a source of weight in order to contribute significantly to the organic matter flux to the deep ocean. Strong global correlations between inorganic minerals (such as CaCO_3 , opal and lithogenic material) and POC fluxes in the deep ocean led to the hypothesis that the denser minerals increased the density, and therefore sinking rate, of POC (the “ballast hypothesis”) (Armstrong et al., 2001; Klaas and Archer, 2002). Deep ocean POC fluxes are thus driven by the local biomineral (i.e. high in calcite-dominated and low in opal-dominated regions.) However, analyses of these relationships on temporal (Lam et al., 2011) and spatial scales (Wilson et al., 2012) have questioned the relative role of minerals as ballast material. The correlations may also reflect other processes governing the association between POC and minerals such as the presence of transparent exopolymer particles (TEP) that stimulate aggregation Passow (2004), De La Rocha et al. (2008). Another explanation for the observed regional POC flux variability is a temperature dependence for the degradation of organic matter. Temperature is a primary determinant for bacterial degradation rates (Gillooly et al., 2001; Matsumoto, 2007) and it has been shown that degradation rates are more sensitive to temperature than photosynthesis (López-Urrutia et al., 2006; Regaudie-de Gioux and Duarte, 2012). Thus, warmer waters are characterised by faster degradation rates and therefore shallower remineralisation (Marsay et al., 2015).

A hypothesis that combines elements of the previous mechanisms specifies ecosystem structure and specifically the extent of recycling of organic matter in the euphotic zone as an important factor governing the observed spatial variability in POC flux (Henson et al., 2012; Le Moigne et al., 2012, 2014). The reasoning is that in high export production areas (generally colder high latitudes) aggregates are rather fresh and loosely packed as they are a result of strong, seasonal diatom blooms, making them prone to rapid degradation. In low export production areas (warmer low latitudes) the material being finally exported has been processed multiple times in the euphotic layer and is therefore tightly-packed, highly refractory and thus experiences reduced microbial degradation at mesopelagic depths (Henson et al., 2012).

An increasing number of mechanisms have been identified that may contribute to changes in the attenuation of POC flux in the water column. However, as highlighted above, these mechanisms are potentially interlinked and difficult to distinguish from current observations. This represents a significant source of uncertainty surrounding the magnitude and sign of ocean carbon cycle feedbacks to changes in atmospheric CO_2 and climate (Barker et al., 2003; Riebesell et al., 2009).

3.2.1.2. Numerical approaches. Most Earth system models impose static POC depth profiles and are therefore based on simple fitting exercises to limited data sets rather than on a mechanistic understanding of the underlying processes. This is surprising, since more sophisticated models have long been used to study organic carbon degradation dynamics in soils and marine sediments over different time-scales (e.g. Arndt et al., 2013). Even though still far from providing an appropriate representation of the plethora of different mechanisms that control organic carbon degradation, these models have proven useful in describing the degradation dynamics of organic carbon from different sources, in different environments, under changing redox-conditions and over time-scales (e.g. Arndt et al., 2013). The applied approaches in ocean biogeochemical models can be broadly divided into two groups: the primarily empirical approaches and more mechanistic approaches of various levels of complexity.

In the early 1980's net primary productivity (NPP) in the surface waters was assumed to be most important for vertical POC flux. The empirical algorithm of Suess (1980) (Eq.(1) in Fig. 6) describes POC flux to depth as a function of NPP, scaled to depth below the sea-surface. However, Bishop (1989) demonstrated that export (or new) production of POC (i.e. POC exported from the euphotic zone) predicts POC flux in deeper waters more reliably and is used until now in biogeochemical models. Other empirically derived relationships used in paleoclimate models are intentionally or unintentionally related to more mechanistic descriptions of organic carbon degradation. Power-law (Martin et al., 1987), single exponential (Volk and Hoffert, 1985; Shaffer, 1996; Heinze et al., 1999) or double exponential (Lutz et al., 2002; Andersson et al., 2004) relationships are applied in most of the paleoclimate models (Table 1). Although these models are usually empirical as well, they can be directly derived from the kinetic first-order rate law of organic matter degradation:

$$\frac{d\text{POC}}{dt} = k \cdot \text{POC} \quad (1)$$

and the chosen function reflects certain assumptions about the organic matter pool and its degradation rate k . Therefore, the representation may be more directly related to some underlying bioenergetic drivers (Berner, 1980b; Boudreau, 1997). The rate constant of organic carbon degradation, k , is usually interpreted as a measure of the reactivity of the macromolecular organic matter towards hydrolytic enzymes and is thus assumed to primarily depend on the macromolecular composition of organic matter. It therefore encompasses not only the original composition of the exported organic carbon, but also its evolution during sinking (Arndt et al., 2013). The simplest form of this approach assumes that the organic carbon constitutes one single pool, which is degraded at a constant rate. This approach is equivalent to the so-called 1G-Model of organic matter degradation (Berner, 1964) that has been widely used in diagenetic modelling (Boudreau, 1997). Its steady-state solution is given by a simple exponential decrease of organic carbon flux with depth that is controlled by the reactivity of organic carbon, k , and the settling velocity, w (Eq.(2) in Fig. 6; see Sarmiento and Gruber, 2006 for a derivation). Yet, this simple exponential model represents merely a linear approximation of the complex degradation dynamics and the first-order degradation constant, k , represents a mean value for the heterogeneous mixture of organic compounds. It should be noted that such simplification is reasonable only if the degradability of different compounds does not vary by more than one order of magnitude (Arndt et al., 2013).

Under the assumption that the organic carbon degradation rate decreases linearly with depth, a power-law functionality for POC flux can be derived from kinetic first-order principles (compare supporting information of Lam et al., 2011). Most commonly used is the description of Martin et al. (1987) – Eq.(3) in Fig. 6. Martin et al. (1987) fitted a number of sediment trap POC flux measurements from six different locations in the northeast Pacific Ocean to a simple power-law. The expression scales deep fluxes to POC export from the euphotic zone