

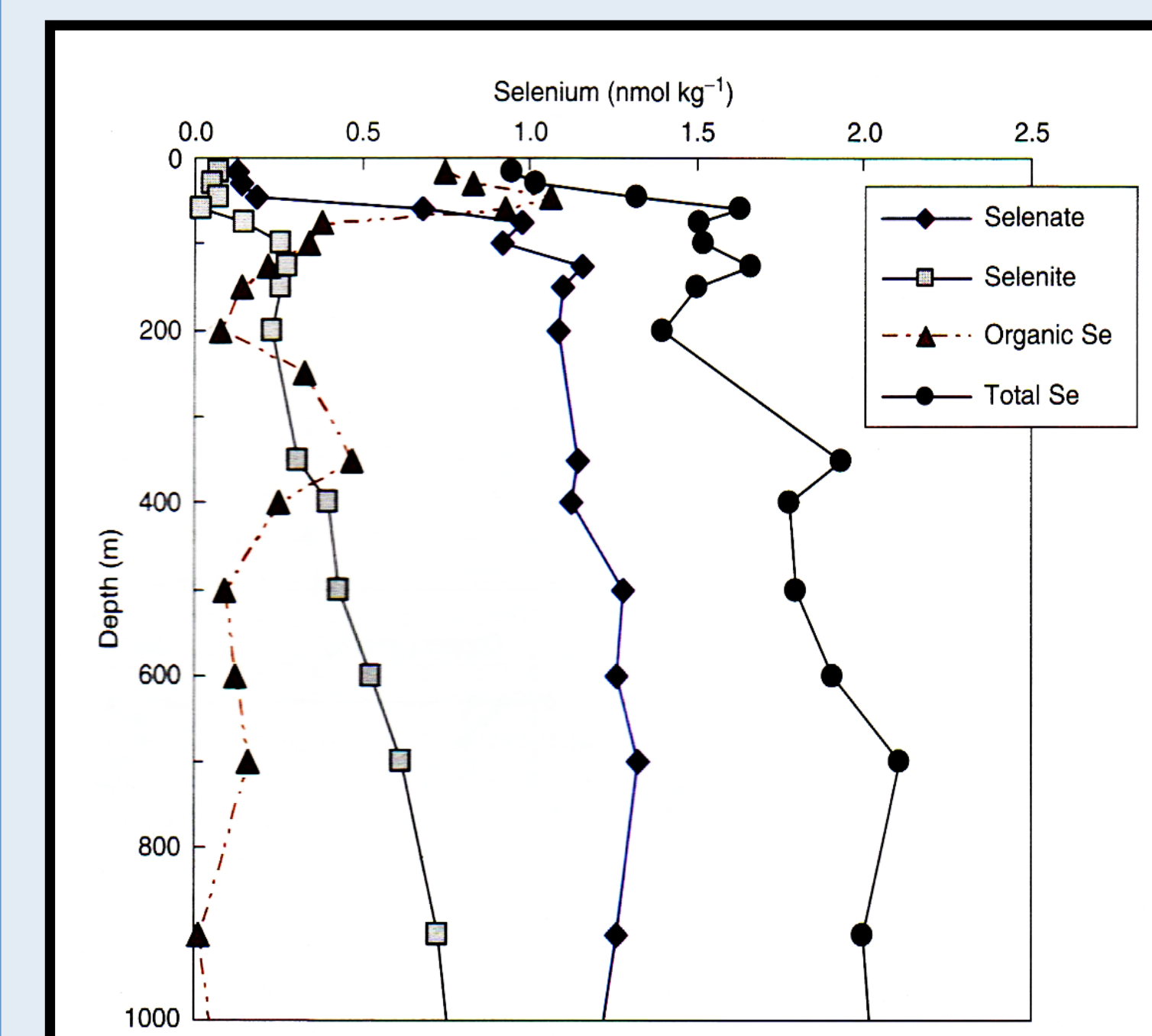
# The Role of Air-Sea Exchange in the Global Selenium Cycle

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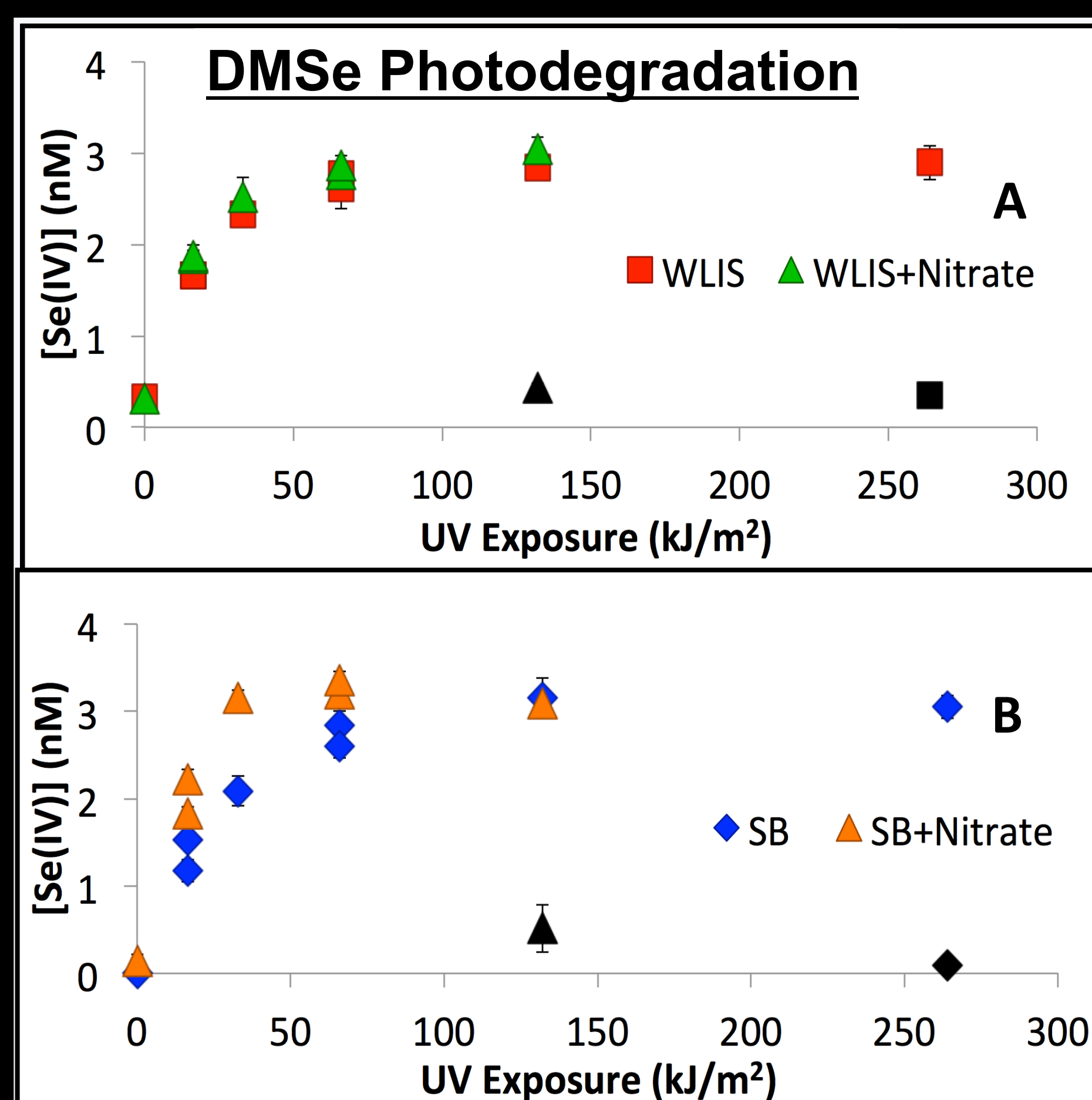
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**Background and Rationale:** Selenium is an important element required by many organisms and is incorporated into seleno-proteins, which contain the essential amino acid, selenocysteine<sup>1</sup>. The biomolecules act as anti-oxidants and mediate cellular redox status. While Se is an essential element it can also be toxic at higher concentrations. In the ocean, phytoplankton produce Se-containing analogs to many sulfur compounds, and the breakdown of these compounds in the surface ocean release volatile methylated Se compounds<sup>2</sup>, such as (CH<sub>3</sub>)<sub>2</sub>Se. Evasion of these compounds to the atmosphere is an important sink for ocean Se and air-sea exchange is an important component of the global Se cycle.<sup>3</sup> Anthropogenic sources of Se rival the inputs from natural processes<sup>3</sup> and therefore concentrations in the biosphere have been exacerbated by human activity. The distribution of Se in the ocean (Fig. 1)<sup>4</sup> illustrates the relative concentrations and distribution in the ocean of the inorganic forms – Se(IV) and Se(VI) – and the total organic Se pool, which includes compounds in the Se(0) and Se(-II) oxidation states. Evidence exists for limitation of plankton growth in some regions of the ocean<sup>5</sup> and genes encoding for Se appear to be ubiquitous in ocean waters<sup>6</sup>. Given the potential importance of these factors in Se cycling and ocean biogeochemistry we examined the potential photochemical processes influencing surface water Se speciation, and developed a global ocean model to examine the processes influencing the ocean distribution of Se, and to assess the current and future impact of human activity on Se in the biosphere.



**Figure 1:** Distribution of selenium throughout the upper ocean<sup>2</sup>.

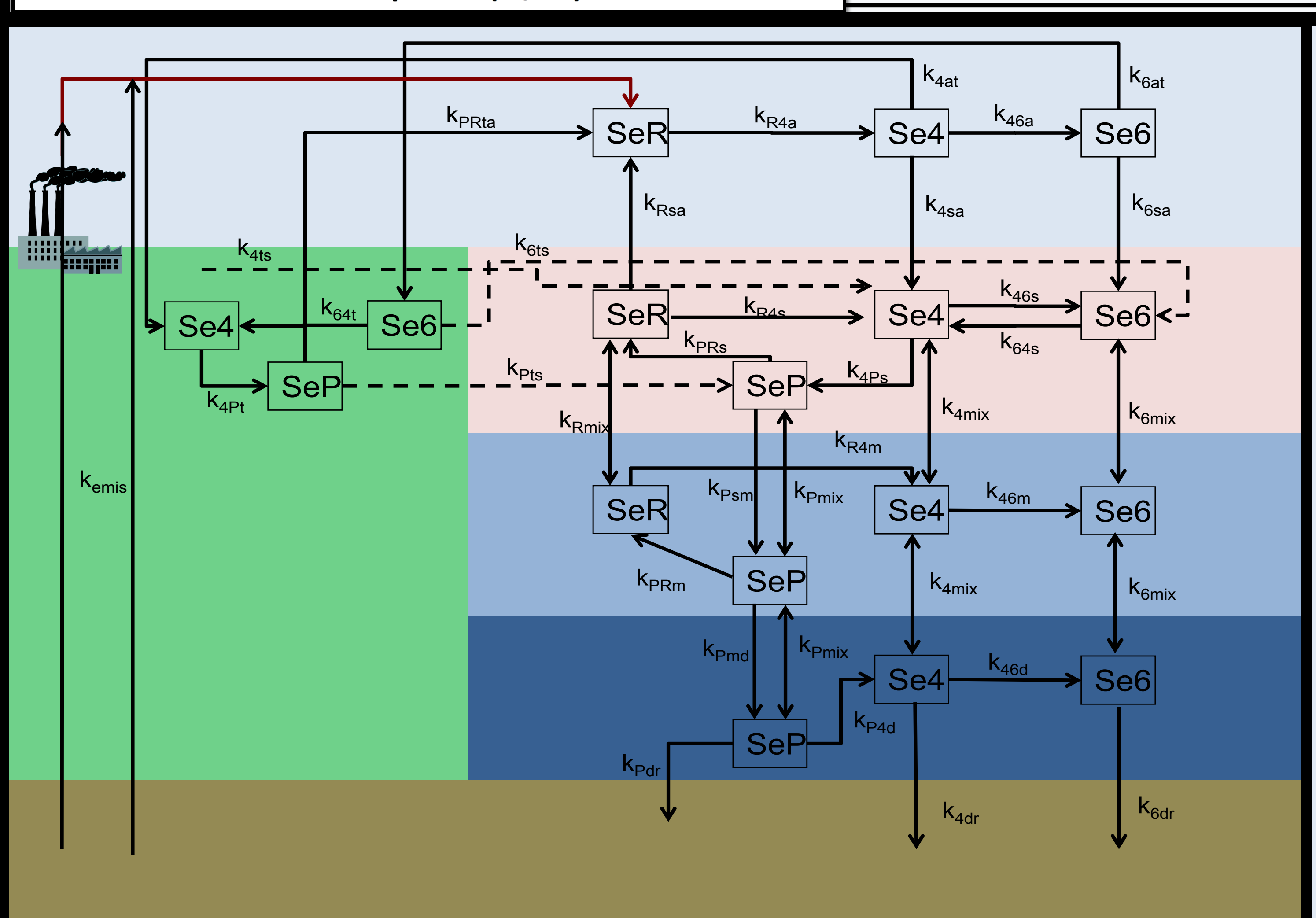


**Figure 2.** Filtered WLIS (A) and SB (B) surface seawater amended to ~3 nM [DMSe] with and without added NO<sub>3</sub><sup>-</sup> (100 μM), exposed to artificial sunlight in quartz vessels for up to 80 minutes. Results are shown as the formation of the degradation product, Se(IV). Colored symbols represent light exposures, black were dark.

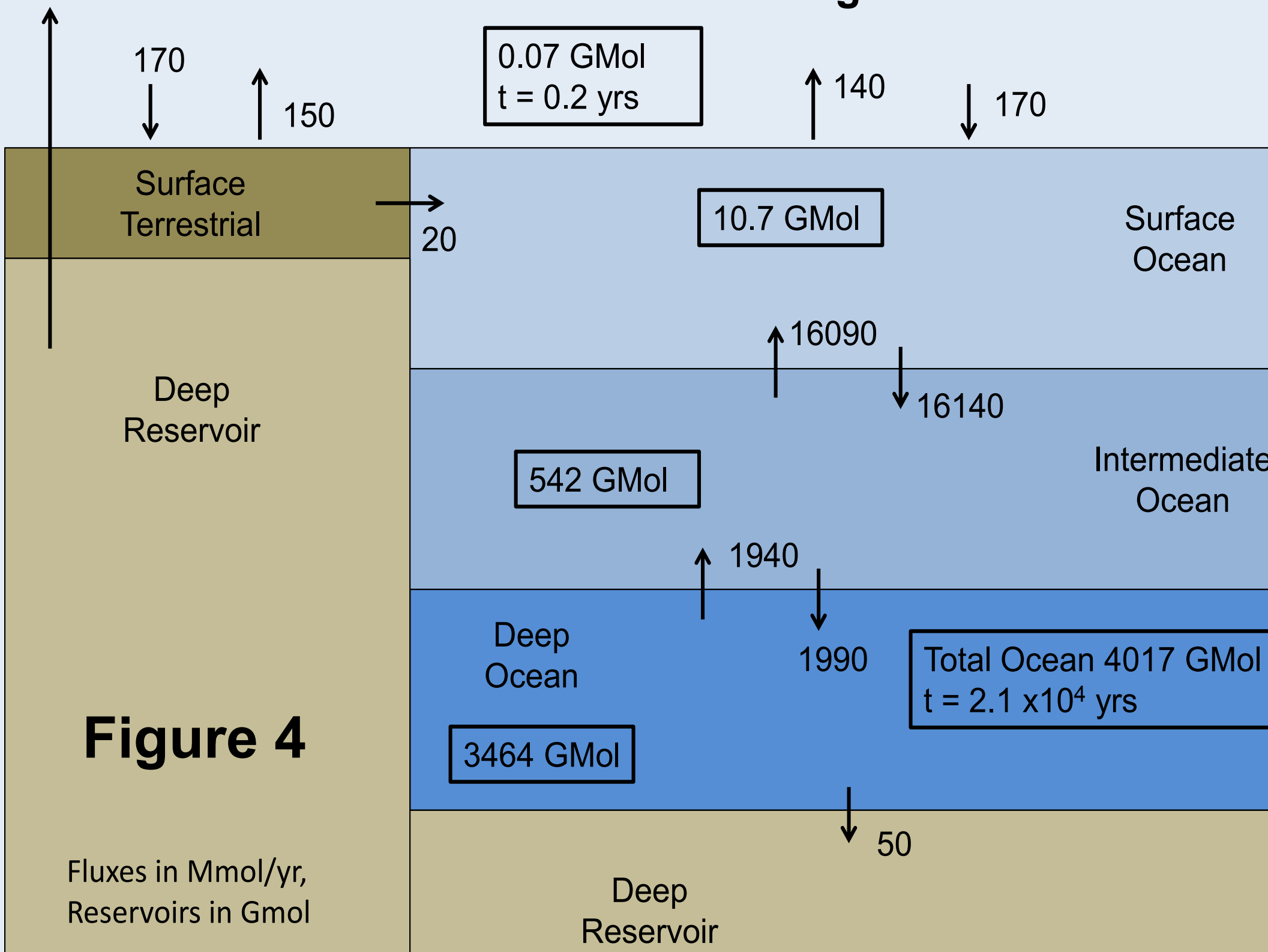
**Figure 3:** Fluxes and reservoirs considered in the global model, developed based on Amos et al.<sup>8,9</sup>

## Results and Discussion

**Photochemical Experiments:** Dimethylselenium is rapidly degraded to Se(VI) in the presence of artificial equatorial sunlight (rates of 10<sup>-3</sup> to 10<sup>-4</sup> s<sup>-1</sup>) (Fig. 2). The rates under natural light and away from the equator, where UV levels are lower, would be slower. However, its instability indicates that most methylated Se is being degraded in the water column rather than evaded to the atmosphere. Our modeling results concur with this observation. In contrast, the photochemical redox transformations of Se(IV) and Se(VI) are much slower with no transformation observed after 6 hours of exposure, suggesting that these processes are not important to the transformation of inorganic Se in the surface ocean. The modeling results (Figs. 4 & 5) suggest however that must be a net mixed layer reduction pathway for Se(VI) otherwise the observed concentration profiles cannot be reproduced. A biotic pathway must exist, mostly likely in association with microorganisms.



## Pre-Industrial Mass Budget



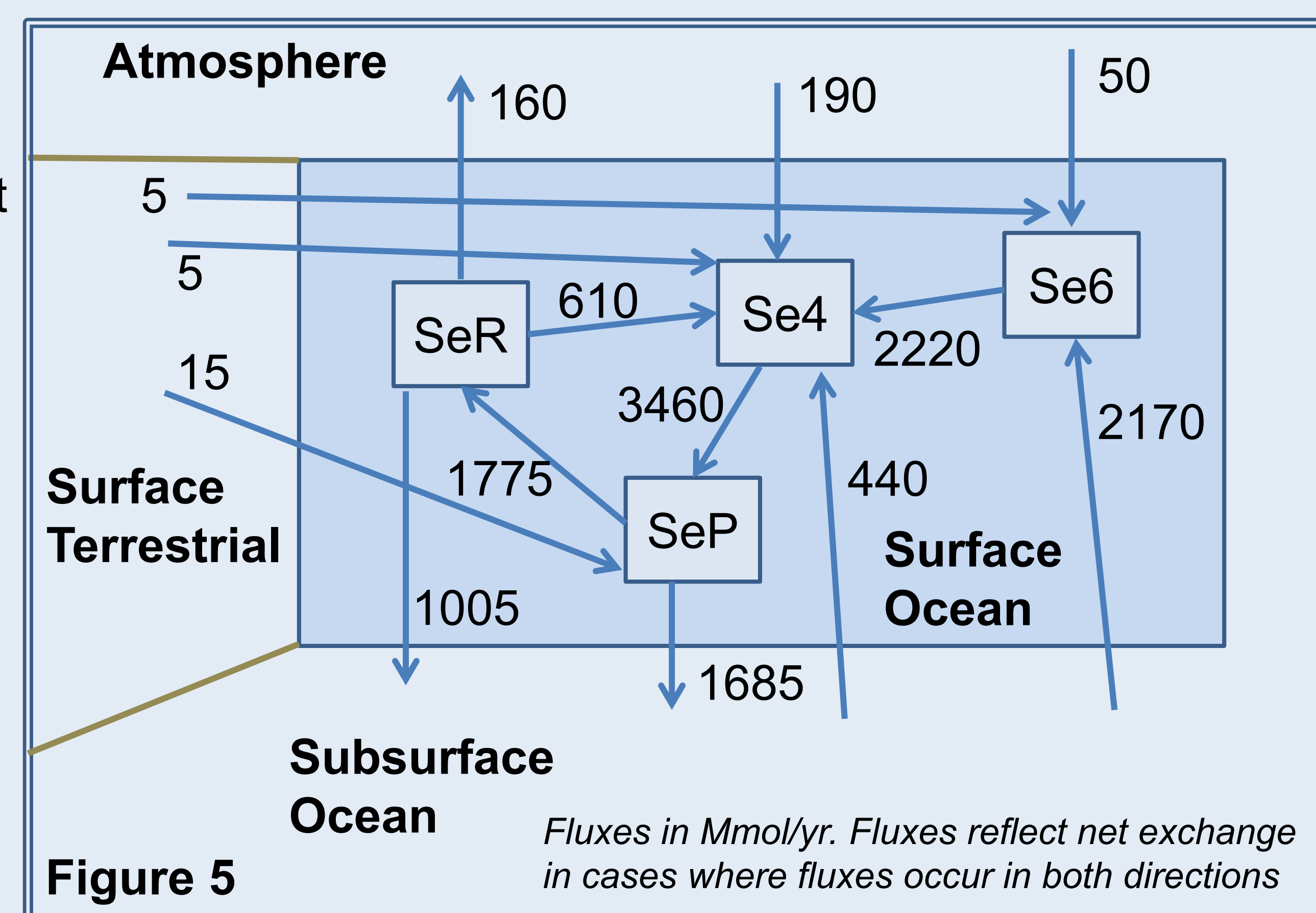
**Pre-Industrial Mass Balance:** Figure 4 illustrates the overall pre-industrial global Se mass balance with fluxes based on the model output for each species. Overall, evasion at the ocean surface is a larger sink than burial in deep ocean sediments. Atmospheric inputs, which include both Se(IV) and Se(VI), are larger than the net input from the terrestrial environment. Overall, the ratio of species in the ocean matches the measurements.<sup>4</sup>

**Anthropogenic Emission Impacts:** Simulations of the impact of anthropogenic emissions since 1850 suggest that human activity has increased the amount of Se in the atmosphere by 35%, and deposition to the ocean by a similar amount. The impact on the ocean is less (10% increase in the surface ocean, 5% increase for the deep ocean), but this is expected given the long residence time of Se in the ocean (2.1 x 10<sup>4</sup> years). Given that the magnitude of the current anthropogenic inputs – 4 times the geogenic inputs in 2008 – the ocean fluxes are no longer at steady state (Fig. 5). In the 2008 simulation, both evasion from the ocean and deep ocean sediment removal have increased by respectively, 15% and 12%.

## Methods:

- Laboratory and Field Studies:** Studies examining the oxidation and reduction of inorganic selenium (both Se(IV) (SeO<sub>3</sub><sup>2-</sup>) and Se(VI) (SeO<sub>4</sub><sup>2-</sup>) and (CH<sub>3</sub>)<sub>2</sub>Se) were carried out using a solar simulator (mimicking midday at the equator) and with natural light at UConn, Avery Point (~41° 21' N). Artificial seawater or water from Eastern (ELIS), Western (WLIS) Long Island Sound, and the North Atlantic continental shelf break (SB) were used for these experiments, all filtered through 0.2 μm filters and stored at 4°C in the dark until use. Dark controls were included for all experiments. Waters were spiked with the specific reactant and then the change in concentration of reactant or product over time was monitored. Exposure time was converted into radiation exposure based on measured light levels, in terms of cumulative UV exposure. Samples were collected and analyzed using standard methods.
- The Se model (Fig. 3) was developed using the framework devised for the global mercury model<sup>8,9</sup>, and the rate coefficients derived from calculations of the inventories for each Se form (Se(IV), Se(VI), organic Se and particulate Se) in the model reservoirs (atmosphere, surface, intermediate and deep ocean, coastal zone and a surface terrestrial layer) and the fluxes between them, estimated for the pre-industrial world. The deep reservoir connects these reservoirs and is the source for geogenic, weathering and anthropogenic inputs of Se. Simulations were completed for the pre-anthropogenic era and for the current era using an emission scenario based on the literature<sup>3</sup> to examine the impact of anthropogenic emissions.

Fig. 5 shows the fluxes in 2008 derived from the model. The net input from the subsurface for Se(IV) and Se(VI) is consistent with ocean profiles (Fig. 1), but overall there is net export to the deep ocean of 80 Mmol/yr. The next reduction of Se(VI) is not photochemical based on our experiments and must reflex a biological process, by bacteria or either on cell surfaces or within cells. **Future work:** Future laboratory studies will examine the mechanism for the reduction of Se(VI). Future modeling will update the model to include a coastal ocean reservoir and further refine the model fluxes through comparison with data.



**Figure 5**

Fluxes in Mmol/yr. Fluxes reflect net exchange in cases where fluxes occur in both directions