Electronic Supplementary Material (ESI) for Metallomics.


**Fig. S1.** Chromatographic separation of the selenium metabolites studied under cation exchange (1st column), reversed-phase (2nd column), and anion exchange chromatographic conditions (3rd column). The figure shows chromatograms of mixtures of standards in water (containing 5.0 µg Se $L^{-1}$ of TMSe, selenosugar 1, and selenosugar 3 for the reversed-phase and cation exchange mixture and 2.0 µg Se $L^{-1}$ of TMSe, selenosugar 1, selenosugar 3, selenite, and selenate for the anion exchange mixture) (1st row), urine collected in the pre-supplementation phase (2nd row), and urine collected in the 400 µg supplementation phase (3rd row). Asterisks indicate the peaks used for quantitation. Selenite was always below the limit of quantitation (0.2 µg Se $L^{-1}$). Selenate levels in the pre-supplementation phase were scattered around the limit of quantitation (0.2 µg Se $L^{-1}$), falling within the range 0.1-0.3 µg Se $L^{-1}$. The column recovery (defined as the percentage of the sum of all peaks eluted from the HPLC column relative to the total urinary selenium) was within the range of 27-41% for the three chromatographic columns and all volunteers under conditions of no supplementation. Column recovery increased upon supplementation due to the dominance of the selenosugars but plateaued at ca. 80% for the 400 µg supplementation phase. Peaks at low retention times (2-4 min) are seen on the cation exchange column and include selenate (RT = 2 min), possibly with other selenium species the identity of which is yet to be established. The contribution of these unknown peaks to the column recovery, however, was small (<5%).