SALTON SEA ECOSYSTEM RESTORATION PROGRAM

Final
Experimental Measurements of Flux of Selenium from Salton Sea Sediments

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EXPERIMENTAL MEASUREMENTS OF FLUX OF SELENIUM FROM SALTON SEA SEDIMENTS

INTRODUCTION

The basic conceptual model for selenium fate, transport, cycling, and bioavailability in the Salton Sea can be characterized as:

1. Loading of oxidized forms of selenium from the rivers and drains,
2. Incorporation of selenium by the lake's biota and conversion into organic selenium,
3. Sedimentation to the lake's bottom (and associated reduction of selenium concentrations in the lake's water column),
4. Decomposition, chemical alteration, and storage of the selenium in sediments (including conversion to chemically reduced forms) as well as diffusive flux of soluble fractions to the water column,
5. Bioaccumulation of sediment selenium into benthic invertebrates, and
6. Transport of bioaccumulated and soluble selenium back from the sediments into the water column and food web.

The implementation of various restoration alternatives and other ongoing changes are likely to alter the influent water quality, volume, depth, and surface area of the Salton Sea. Such changes are likely to result in a net change in the conditions at the sediment/water interface. Future conditions are likely to include various levels of decreased salinity of the water overlying some of the lake's sediment. Increased or decreased oxygenation of overlying water and altered wave-driven sediment resuspension (from the changed water depth and fetch of a smaller lake) are all possible under future conditions. It is likely that the balance between riverine loading and internal supply as sources of selenium to the Salton Sea biota also will change.

The synoptic distribution of selenium in surface sediment is fairly well known from historical samples (Vogl and Henry, 2002; Schroeder et al., 2002; Schroeder and Orem, 2000) as well as the more recent analyses from extensive sampling in 2003 and 2005. In addition, the chemical character of influent rivers and the water column has been described (Setmire et al., 1993; Setmire and Schroeder, 1998), and monitoring continues to the present (including selenium speciation). Such characterizations describe the inventory of selenium as described by the line items of the conceptual model, above (major portions of items 1 – 5). However, the role of the Salton Sea sediment selenium in affecting water column concentrations and selenium bioavailability is relatively unknown (point 6, above). Given the large inventory of selenium in Salton Sea sediments and the importance of sediment flux and invertebrate bioaccumulation, it is possible that changing the lake mixing, oxygen content, and water quality may alter the flux of selenium from the sediments and affect the bioavailability of selenium in the system.

The experiment described here was designed to measure selenium flux from sediments into overlying water under controlled, laboratory conditions that mimic current and potential future Salton Sea conditions. The experiment was based on proven techniques and analogous designs that have been applied to the Salton Sea and other sediments in attempts to measure nutrient flux.

It is expected that at some point all such core experiments might diverge significantly from the conditions of the natural lake but that short-term experiments should provide a valid estimate of selenium flux. Flux from sediment cores is expected to be linear in the short term and to gradually taper off to an asymptotic value when the sediment and overlying water reach a new equilibrium. These long-term, final equilibrium conditions would represent laboratory artifacts that were dictated by the relative surface area and volume of the sediment and overlying water in the test cores (i.e., heavily influenced by experimental design). Instead, we measured the short-term selenium flux as being more indicative of differences among experimental conditions and an adequate mimic of field conditions for current purposes. In addition, the daily sampling and replacement of approximately one-fourth of the overlying water volume prevented high concentrations of selenium and other constituents from artificially building up and altering the sediment/water concentration gradients that determine diffusive flux.

METHODS

The experiment was constructed as a 3 X 2 factorial design with three replicates per condition. The sediment was collected as 18 intact cores with overlying water from a localized area of the northern basin of the Salton Sea to minimize inter-core variability (all from 25 feet of water depth). The cores were brought into the laboratory and each was subjected to one of three new, overlying water salinities (35 ppt, 20 ppt, or 2 ppt). The overlying water of each of those three conditions was modified to be either anoxic (N_2 bubbled to remove dissolved oxygen) or to be oxygen-saturated (air bubbled). Three replicates were prepared for each condition, resulting in 18 cores total (3 salinities * 2 oxidizing conditions * 3 replicates = 18 cores).

Following the basic, successful field collection and laboratory handling protocols of Anderson and Amrhein (2002) and Beutel (2001), the 8-cm by 30-cm cores were collected using a tall Ekman dredge. When carefully handled, a single intact sediment core with 9.5 - 23 cm of sediment and 25 - 30 cm of overlying water was collected by hand coring and capping within each Ekman dredge haul. The cores were capped on top and bottom and completely filled with site water at the time of collection. They were then held vertically and transported on ice to the laboratory with no obvious evidence of sediment/water mixing (i.e., similar to techniques of Beutel, 2001). It is assumed that the sediment of all 18 cores would be fairly similar, containing porewater concentrations at the start of the experiment in equilibrium with the overlying lake water of approximately 45 ppt salinity. Although variable in total sediment volume per core, the sediment volumes were not statistically different as related to final core conditions of salinity or aeration (ANOVA, $P > 0.05$). Sediment selenium concentrations were measured from the homogenized sediment of each core at the end of the experiment to measure inter-core variability. In addition, a single surface sediment sample was collected in the field from the immediate area and at the same time as the cores were collected to serve as a representative “Time 0” sediment characterization.

Stock water solutions were created for the 35 and 20 ppt laboratory conditions by diluting net-filtered Salton Sea water with distilled water. The lake water was field-filtered using plankton netting to remove the zooplankton and larger phytoplankton using 80 um mesh netting. In contrast, the 2 ppt stock water was created by mixing commercially-available aquarium salts (Oceanic Natural Sea Salt Mix®) with laboratory distilled water. It was assumed that future freshwater alternatives would be characterized by treated river water overlying older, Salton Sea sediments rather than by diluted lake water. Future river treatments were assumed to be designed to remove selenium. Therefore, Alamo or New River waters (untreated) would not have been appropriate for use as the low-salinity condition because they would be likely to have added too much selenium to the overlying water. All salinities of stock waters and cores were checked daily using a calibrated EC meter. The stock solutions were sampled to verify total selenium concentrations at the end of the experiment.

In the laboratory, all overlying water of the cores was replaced by gentle siphoning and adding back the desired salinity water followed by aeration of water overlying all cores for 24 hours as a pre-leaching. The pre-leaching water was assessed for total selenium content at the end of the one-day period. Preliminary experiments with intact Salton Sea cores had indicated that the salinity of the overlying water stabilized after 4 - 6 hours of leaching. All cores were held in the dark at approximately 19 - 20° C except for brief periods each day when they were sampled and stock water was added to bring them back to their original volume.

At Time 0 of the experiment all core chambers were completely refilled in the laboratory with water of their assigned salinity (diluted Salton Sea water [35 ppt or 20 ppt] or artificial seawater [2 ppt]), and gentle air or N_2 gas bubbling was started (to induce continuous mixing of the water with the sediments without obvious sediment resuspension). Starting at Day 1 after the start of the experiment, the overlying water was sampled for total selenium concentration by removal of a subsample and addition of a comparable volume of stock water. The cores were similarly sampled each day at 24-hour intervals for 5 days. The overlying water of the last sample (Day 5) was analyzed for total and dissolved selenium, including selenate, selenite, and organic selenium concentrations in the dissolved fraction. The 5-day span of the experiment was chosen based on the linear results of nutrient flux from Salton Sea sediment cores observed over that same time period (Anderson and Amrhein, 2002). The amount of sediment and water in each core and assignments of experimental conditions are given in Table 1. Sediment selenium concentration for each core also is included in Table 1, as discussed in methods and results, below.

At the end of the experiment, the sediment from each of the cores was analyzed for total selenium concentration, total organic carbon (TOC), and grain size. Such analyses helped in interpreting uncontrolled sources of variability (see results, below). No benthic organisms were observed in the cores that might have influenced inter-core variability. All cores arrived from the field with a light, white bacterial layer on the top of the sediments that was apparent in all freshly-collected material. Only the cores maintained as anoxic retained that obvious bacterial layer through to the end of the experiment.

The flux of total selenium from (or into) the sediment was estimated from the concentration results by knowing the concentration and volumes of both sampled and added water on a daily basis and following the estimated load in the overlying water of the individual cores over time. The total overlying water load of Day (n+1) subtracted from load at Day (n) represented the increased load over the previous 24 hours (daily flux). Cumulative flux was simply estimated by adding the daily fluxes sequentially over the 5-day experiment to get a rate for the 5-day total. There wasn't enough volume of overlying water to sample for selenium speciation daily; therefore, selenium speciation results are presented as concentrations in the overlying water of each core on Day 5 of the experiment (when the cores were drained to take the final samples). The speciation results show qualitative differences in speciation among test groups, but not load or flux. Flux of individual selenium species may be assumed for each core on Day 5 as a proportion of the flux of total selenium.

It was not possible in this experiment to estimate the loss of volatile selenium species. However, comparative studies suggest that volatile selenium losses from pond sediments range from 0.6 to 2.4 percent of input selenium (Frankenberger and Karlson, 1994). Any differential losses of volatile fractions are assumed to be small but unaccounted in this experiment.

RESULTS

The results provide estimates of the rate of total selenium loss from (positive flux) or gain to (negative flux) the sediments under the three salinities and two dissolved oxygen regimes. The results are presented as graphs of the selenium flux from the sediments over time (µg/cm^2/day) for the three different salinity conditions in Figures 1a, b, and c. Positive values indicate selenium loading from the sediment into the overlying water; negative values are the net loss of overlying water load over the course of a day. Figures 2a, b, and c show the same positive/negative flux results as cumulative flux that adds each day (from Figure 1) to the sum of all previous days. Tables 2 and 3 present the results of ANOVA comparisons documenting statistically significant cumulative flux differences (Table 2) and selenium concentrations (Table 3) in the various treatment conditions.

Initial, aerated pre-leaching of all cores prior to the start of the experiment yielded the greatest selenium from the 2 ppt cores (0.014 µg Se/cm^2/day), followed by 35 and 20 ppt conditions (0.002 and 0.001 µg Se/cm^2/day, respectively). This result was expected based on simple diffusive loss of salts from the sediment porewater that was in equilibrium with field conditions at the start of the leaching (i.e., approximately 45 ppt Salton Sea water). The magnitude of diffusive loss of salts (including selenium compounds) from the sediment would be expected to be generally related to the difference in salt concentrations between the new overlying water and the sediment porewater, but the difference in initial leaching between 20 and 35 ppt conditions was not significant. Monitoring of electrical conductivity over the course of the experiment revealed that the cores did not increase significantly in bulk salinity during the next five days; the pre-leaching allowed the cores to be held in their experimental salinity conditions over the remainder of the experiment.

Several characteristics of the results are immediately apparent from an examination of Figures 1 and 2.

- For all three salinity conditions, the aerated cores tended to yield the higher and more positive fluxes (e.g., Figure 1a). The higher cumulative fluxes and positive trends in flux over time were also shown as predominately from the aerated cores (Figures 2a, b, c).
- A second major trend that is evident from Figure 1 is that while the 2 ppt condition yielded mostly positive fluxes over the 5-day experiment, the higher salinity conditions were less consistent; they both produced positive flux rates peaking on Day 3 (Figure 1b, c; Figure 2b, c).
- A third characteristic is that the negative and positive fluxes over all conditions are almost equivalent, resulting in mostly positive cumulative fluxes for the 2 ppt condition (Figure 2a) and mostly negative cumulative fluxes for the more saline conditions (Figures 2b, c).

The statistical evaluation of the experimental results verified the trends described above. The cumulative flux and final concentrations of selenium in the overlying water of the cores were influenced by both the salinity of the overlying water and the aeration of the cores. In general, aerated conditions yielded the greatest flux of selenium from the intact cores and the lowest-salinity overlying water had the largest positive flux of selenium out of the sediment (Table 2).

The concentrations of selenium fractions and species in the overlying water at the end of the experiment were used as an additional measure of net sediment/water interactions. In contrast to the trend in total flux to the overlying water at 2 ppt, the concentrations of total selenium in the overlying water at the end of the experiment were lower for the lowest salinity condition (Table 3); this is likely a result of the presence of Salton Sea selenium in the 20 and 35 ppt overlying water (partially replaced on a daily basis) versus the lack of selenium in the 2 ppt non-Salton Sea replacement water. This lower concentration effect in the 2 ppt condition was also evident for dissolved organic selenium, and for total dissolved selenium. In contrast, dissolved selenite did not exhibit effects due to salinity, and selenate was uniformly not detected (Table 3).

There were aeration effects on the final selenium concentrations, as well. The aerated cores yielded higher total selenium and dissolved selenite concentrations but lower for organic fractions as compared to the anoxic cores (Table 3).

The estimated areal loading rate from aerated and anaerobic sediments, shown as the mean, cumulative rate over the 5-day experiment is given in Figure 3. Note the consistent differences between aerated and anoxic conditions and positive fluxes limited to the freshwater condition (2 ppt). In contrast, both saline conditions demonstrated a net loss of selenium from the overlying water to the sediments over the course of the experiment (although, following an initial positive value during pre-leaching, see above).

Variability in the selenium content and other sediment characteristics among cores was not related to the pattern of flux results. Sediment selenium concentrations measured at the end of the experiment showed no statistically different concentrations among experimental groups. In addition, there was no statistically significant relationship between selenium flux and the selenium content of the bulk sediment.

Selenium flux (positive or negative) between the sediments and water was statistically unrelated to the volume of sediment in the core, sediment grain size, or sediment TOC. However, total selenium concentration of the sediment in the cores was significantly related to TOC and to grain size (higher selenium occurred in sediments of finer grain size and higher TOC content) (Linear regression, $P < 0.05$). This general characteristic has been described before for Salton Sea sediments (Schroeder et al., 2002).

CONCLUSIONS

The results from the intact core experiments tend to verify the known behavior of selenium in the aquatic environment and, particularly, in terms of selenium interactions between water and sediment. Anoxic conditions have been cited as favoring low redox values that promote the formation of insoluble compounds of selenium and would promote the retention of selenium in the sediment versus the overlying water (Masscheleyn and Patrick, 1993). This result was verified by the higher flux to overlying water and higher water concentrations for the aerated conditions as compared to anoxic cores (Tables 2 and 3, Figures 1 - 3). However, despite this trend for aeration, higher salinities tended to promote a net loss of selenium from the water (Table 2, Figure 3).

The implications of this result are that selenium stored in the lake's sediment is likely to be released into the overlying water if the sediment-water interface becomes increasingly oxygenated as part of future, freshwater wetlands (2 ppt). Shallow, freshwater wetlands would be expected to be more aerated than the current lake and this experimental result suggests that there is some enhanced potential for selenium loss to overlying waters for that future, shallow, freshwater condition as compared to current lake conditions.

A directional trend was evident for the more saline conditions in that all net fluxes were negative. The directional trend also supports the literature-based concept that aeration of chronically-anoxic sediments will promote the release of sediment-bound selenium. Although aerated conditions produced less negative fluxes than reduced conditions (e.g., Figures 1 - 3), it is not possible from this experiment to estimate an increased selenium flux to the overlying water that might be directly related to improved water quality (more oxygenation) of future, saline lake conditions (20 or 35 ppt).

The comparison of selenium concentrations among overlying water salinities is supportive of the intuitively obvious concept that greatly reduced salinity (2 ppt condition) will leach more salts (and selenium) from saline sediments than would salinities closer to the original lake-bed salinity (the 20 and 35 ppt conditions). In general, the 2 ppt expected condition was the only set of cores showing consistent positive flux of total selenium over the course of the experiment (Figures 1 - 3). The 2 ppt condition yielded a greater total flux (Table 2) but lower concentrations of constituents in the overlying water (Table 3). This latter result is undoubtedly related to the selenium-free nature of the 2 ppt replacement water in contrast to the diluted Salton Sea water of the other, more saline conditions. Therefore, fluxes (rather than water concentrations measured at the end of the experiment) are probably the best indicator of sediment behavior.

It is expected that flooding of new wetlands with treated river water over Salton Sea sediments will leach selenium from the sediments as a result of the strength of the diffusive salinity gradient from porewater and the tendency towards aerobic conditions in shallow, windswept water bodies. For future saline conditions (20 or 35 ppt overlying waters) it is less likely that selenium will be drawn from the sediments.

REFERENCES

Anderson, M.A., and C. Amrhein. *Nutrient Cycling in the Salton Sea.* Final Report to Salton Sea Authority, Dept. of Environ. Sci., Univ. Calif. Riverside. 2002.

Beutel, M.W. Oxygen consumption and ammonia accumulation in the hypolimnion of Walker Lake, Nevada. *Hydrobiologia* 466:107–117. 2001.

Frankenberger, W.T., Jr., and U. Karlson. Microbial volatilization of selenium from soils and sediments. Pages 369-388. In Frankenberger, W.T., Jr., and S. Benson (eds.) *Selenium in the Environment.* Marcel Dekker, Inc., New York. 1994.

Masscheleyn, P.H., and W.H. Patrick. Biogeochemical processes affecting selenium cycling in wetlands. *Environ. Toxicol. Chem.* 12:2235-2243. 1993.

Schroeder, R.A., W.H. Orem, and Y.K. Kharaka. Chemical Evolution of the Salton Sea, California: Nutrient and Selenium Dynamics. Pages 23-45. In Barnum, D.A., J.F. Elder, D. Stephens, and M. Friend (eds.) *Developments in Hydrobiology* 161, Kluwer Academic Publishers. 2002.

Schroeder, R.A., and W.H. Orem. Nutrient dynamics in the Salton Basin - Implication from Calcium, Uranium, Molybdenum, and Selenium. Poster presented at Spring 2000 Annual Meeting, American Geophysical Union, Washington, D.C. 2000.

Setmire, J.G., R.A. Schroeder, J.N. Densmore, S.L. Goodbred, D.J. Audet, and W. R. Radke. Detailed Study of Water Quality, Bottom Sediment, and Biota Associated with Irrigation Drainage in the Salton Sea Area, California, 1988-90. U.S. Geological Survey, Water Resources Investigations Report 93-4014. 1993.

Setmire, J.G., and R.A. Schroeder. Selenium and Salinity Concerns in the Salton Sea Area. Pages 205-222. In Frankenberger, Jr., W.T. and R.A. Engberg (eds.) *Environmental Chemistry of Selenium*, Marcel Dekker, Inc. 1998.

Vogl, R.A., and R.N. Henry. Characteristics and Contaminants of the Salton Sea Sediments. Pages 47-54. In Barnum, D.A., J.F. Elder, D. Stephens, and M. Friend (eds.) *Developments in Hydrobiology 161*, Kluwer Academic Publishers. 2002.

TABLES

Table 1
Experimental Assignments and Conditions for Each of the 18 Cores

Core	Sediment Height (cm)	Sediment Selenium (mg/kg DW)	Overlying Water Salinity (ppt)	Aeration Condition	Overlying Water Volume (L)
1	14.5	6.19	2	O2	1.14
2	23.0	8.02	2	N2	1.05
3	20.5	7.14	2	O2	1.09
4	21.0	6.66	2	N2	1.09
5	21.5	8.66	2	O2	1.14
6	19.5	5.57	2	N2	1.14
7	20.5	6.75	20	O2	1.14
8	17.5	8.44	20	O2	1.14
9	9.5	6.58	20	N2	1.14
10	21.0	3.78	20	N2	1.09
11	21.75	8.16	20	O2	1.09
12	17.0	9.09	20	N2	1.14
13	21.0	5.55	35	N2	1.09
14	17.5	8.39	35	O2	1.14
15	19.5	7.28	35	N2	1.14
16	19.0	8.00	35	O2	1.14
17	13.75	10.60	35	O2	1.14
18	21.75	7.71	35	N2	1.14

Table 2
Tests of Significance for Differences among Experimental Groups, Showing Effects of Salinity and Aeration on Flux of Selenium in the Overlying Water of the Intact Cores. ANOVA on Log-transformed or Raw Results, with Statistically Significant Differences at P < 0.05.

Comparison	Means of Tested Values (Flux = µg Se/core/day)	Overall ANOVA Results	Detailed Comparisons
Day-3 Cumulative Flux	Oxygenated: 2 ppt = 0.257 20 ppt = -0.078 35 ppt = -0.065 Anoxic: 2 ppt = -0.108 20 ppt = -0.217 35 ppt = -0.350	Significant effects due to both aeration and salinity.	Aerated condition = higher flux. 2 ppt condition = higher flux than 35 ppt.
Day-5 Cumulative Flux	Oxygenated: 2 ppt = 0.469 20 ppt = -0.231 35 ppt = -0.217 Anoxic: 2 ppt = 0.048 20 ppt = -0.397 35 ppt = -0.805	Significant effects due to both aeration and salinity.	Aerated condition = higher flux. 2 ppt condition = higher flux than 20 or 35 ppt.

Table 3

Tests of Significance for Differences among Experimental Groups, Showing Effects of Salinity and Aeration on the Concentration of Selenium in the Overlying Water of the Intact Cores. ANOVA on Log-transformed or Raw Results, with Statistically Significant Differences at P < 0.05.

Comparison	Means of Tested Values (Concentration = µg Se/L)	Overall ANOVA Results	Detailed Comparisons
Day-5 Total selenium concentrations	Oxygenated: 2 ppt = 0.275 20 ppt = 0.640 35 ppt = 1.074 Anoxic: 2 ppt = 0.161 20 ppt = 0.638 35 ppt = 0.731	Significant effects due to both aeration and salinity.	Aerated condition = higher concentrations. 2 ppt condition = lower concentrations than 20 or 35 ppt. 20 ppt condition = lower concentrations than 35 ppt.
Day-5 Total dissolved selenium concentrations	Oxygenated: 2 ppt = 0.271 20 ppt = 0.614 35 ppt = 0.947 Anoxic: 2 ppt = 0.172 20 ppt = 0.744 35 ppt = 0.828	Significant effects due to salinity only.	2 ppt condition = lower concentrations than 20 or 35 ppt. 20 ppt condition = lower concentrations than 35 ppt.
Day-5 Dissolved selenate (Se+6) concentrations	Oxygenated: 2 ppt = ND 20 ppt = ND 35 ppt = ND Anoxic: 2 ppt = ND 20 ppt = ND 35 ppt = ND	All results below detection limits.	All results below detection limits.
Day-5 Dissolved selenite (Se+4) concentrations	Oxygenated: 2 ppt = 0.142 20 ppt = 0.228 35 ppt = 0.280 Anoxic: 2 ppt = 0.042 20 ppt = 0.060 35 ppt = 0.181	Significant effects due to aeration only.	Aerated condition = higher concentrations than anoxic.
Day-5 Dissolved organic selenium concentrations	Oxygenated: 2 ppt = 0.128 20 ppt = 0.386 35 ppt = 0.666 Anoxic: 2 ppt = 0.130 20 ppt = 0.684 35 ppt = 0.647	Significant effects due to salinity and aeration.	2 ppt condition = lower concentrations than 20 or 35 ppt. 20 ppt condition = lower concentrations than 35 ppt. Aerated condition = lower concentrations than anoxic.

FIGURES

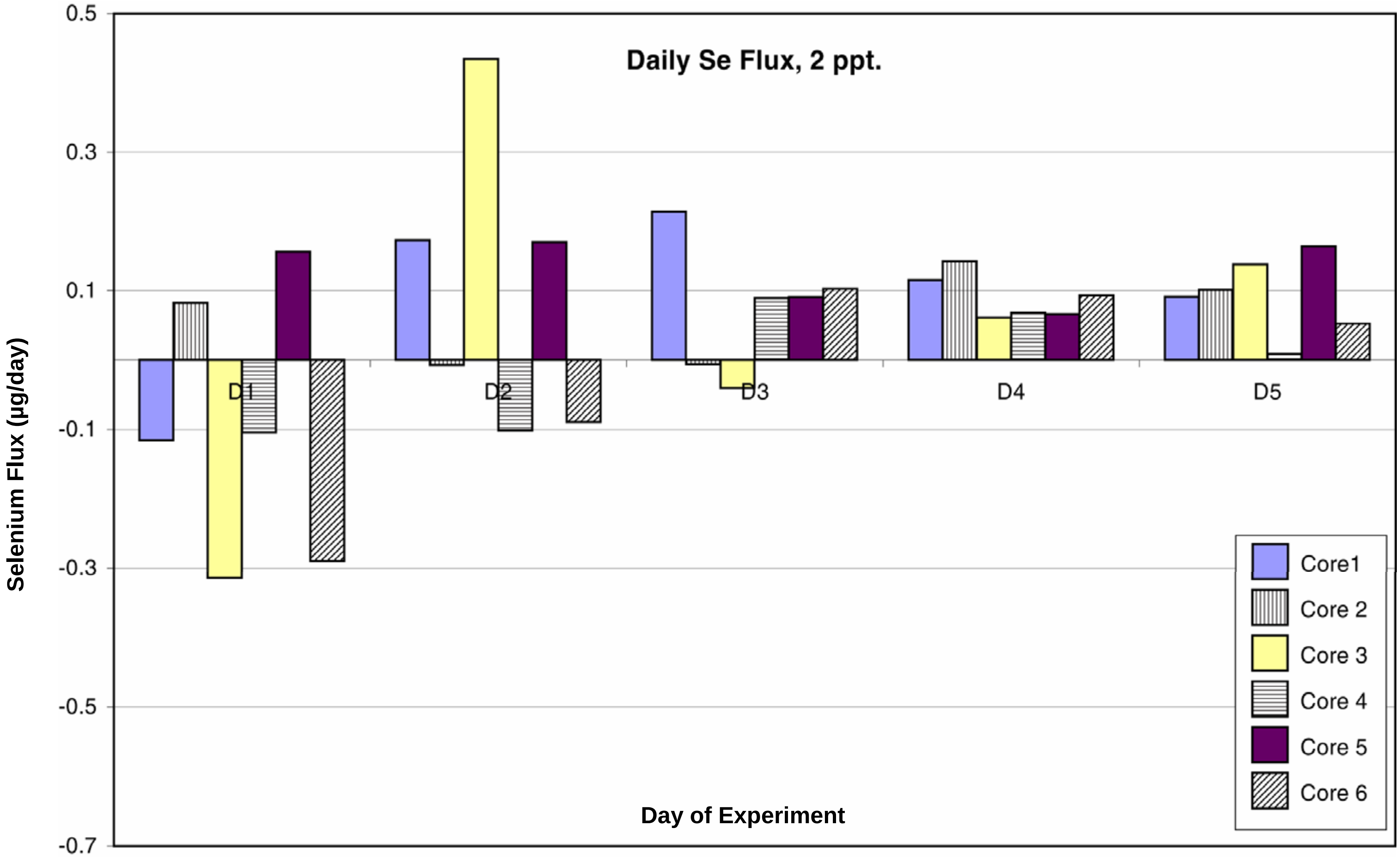

Figure 1a
Daily Selenium Flux over the 5-day Experiment at 2 ppt Overlying Water. Solid Bars Were Aerated Cores, Hatched Bars Were Anoxic

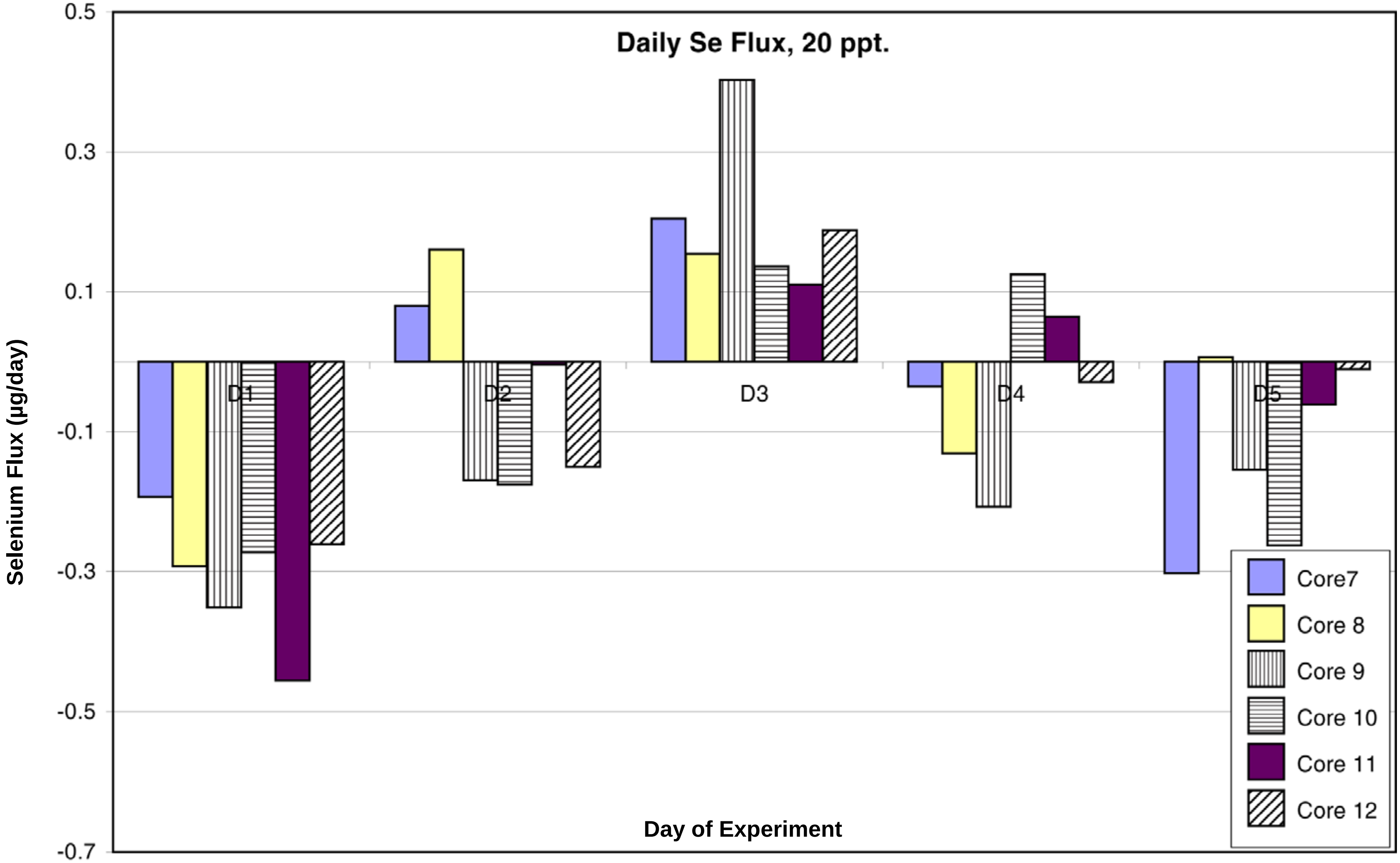

Figure 1b

Daily Selenium Flux over the 5-day Experiment at 20 ppt Overlaying Water. Solid Bars Were Aerated Cores, hatched Bars Were Anoxic.

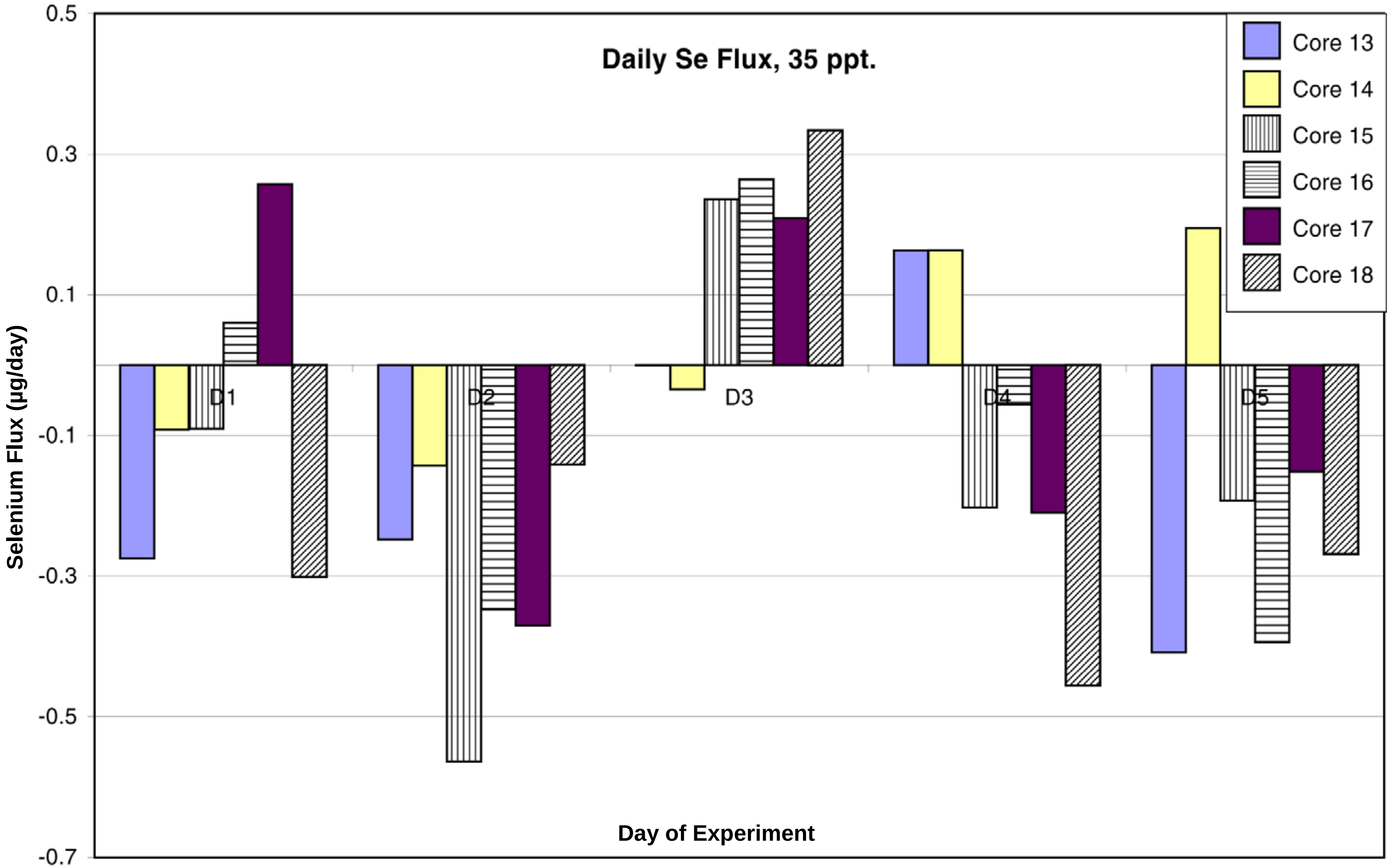

Figure 1c

Daily Selenium Flux over the 5-day Experiment at 35 ppt Overlaying Water. Solid Bars Were Aerated Cores, Hatched Bars Were Anoxic.

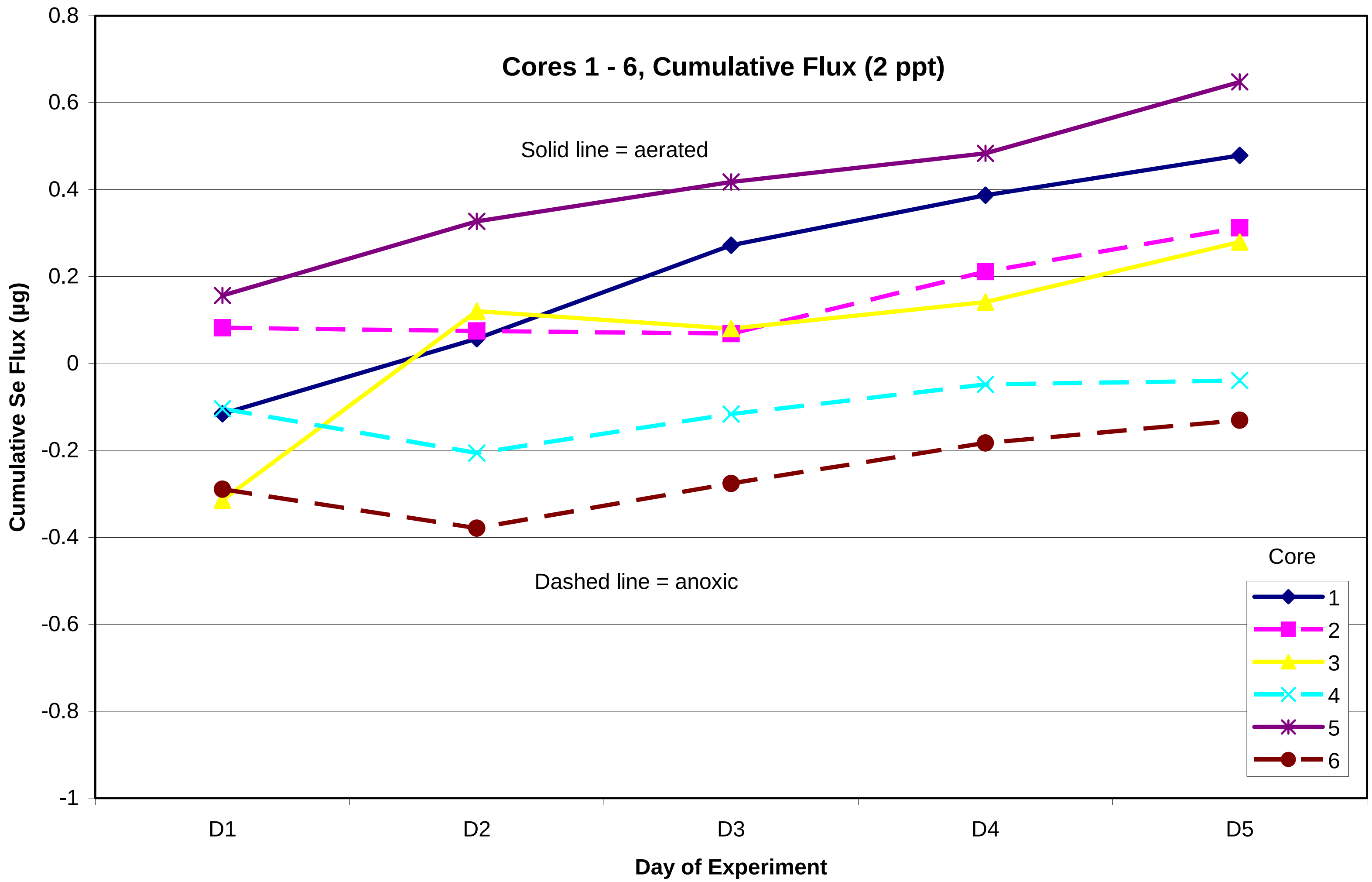

Figure 2a
Cumulative Selenium Flux over the 5-day Experiment Shown as Load/Core from the Sediment (+ Values) or into the Sediment (- Values) for 2 ppt Overlying Water. Aerated Cores Are Solid Lines, Anoxic Cores Are Dashed Lines.

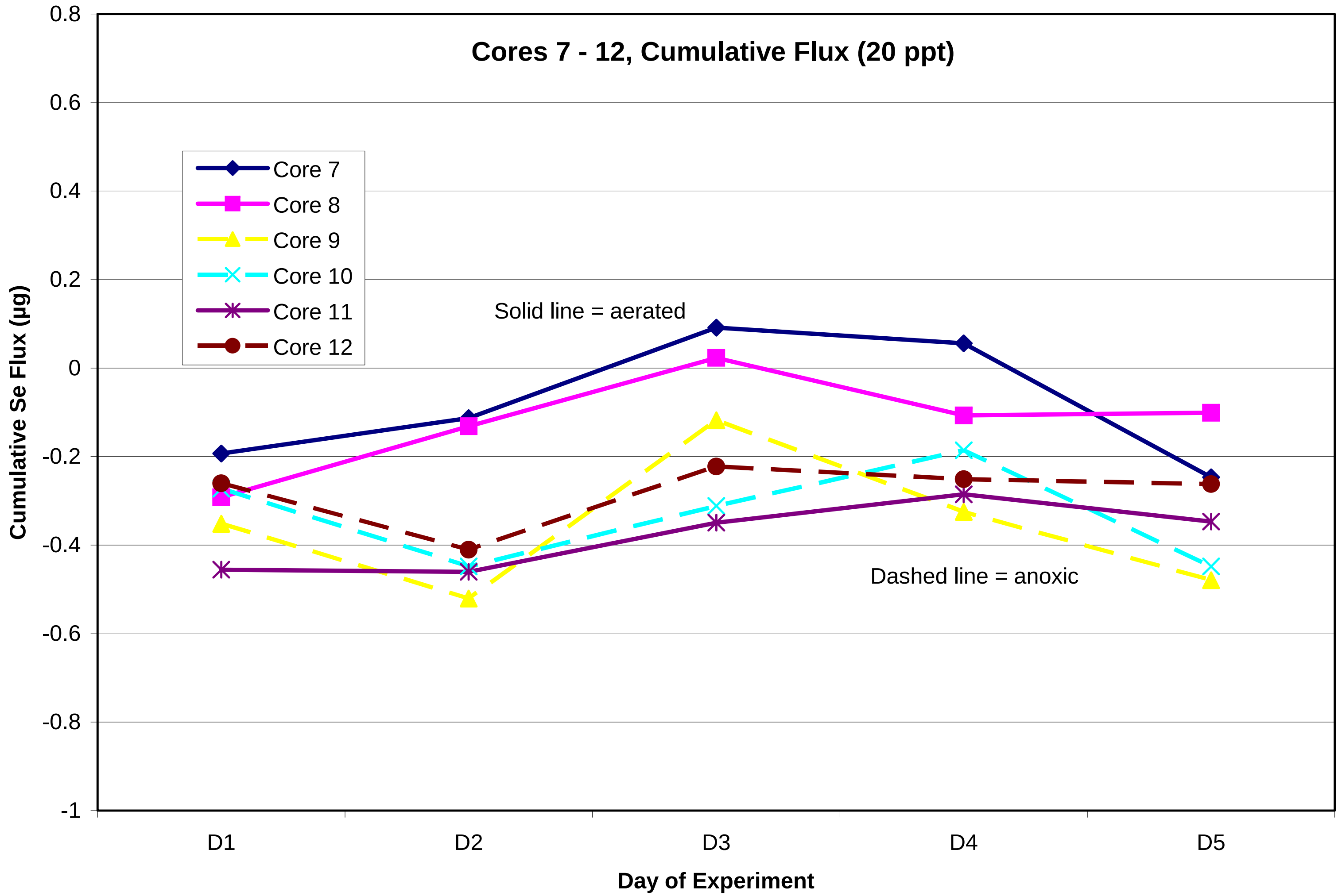

Figure 2b
Cumulative Selenium Flux over the 5-day Experiment Shown as Load/Core from the Sediment (+ Values) or into the Sediment (- Values) for 20 ppt Overlying Water. Aerated Cores Are Solid Lines, Anoxic Cores Are Dashed Lines.

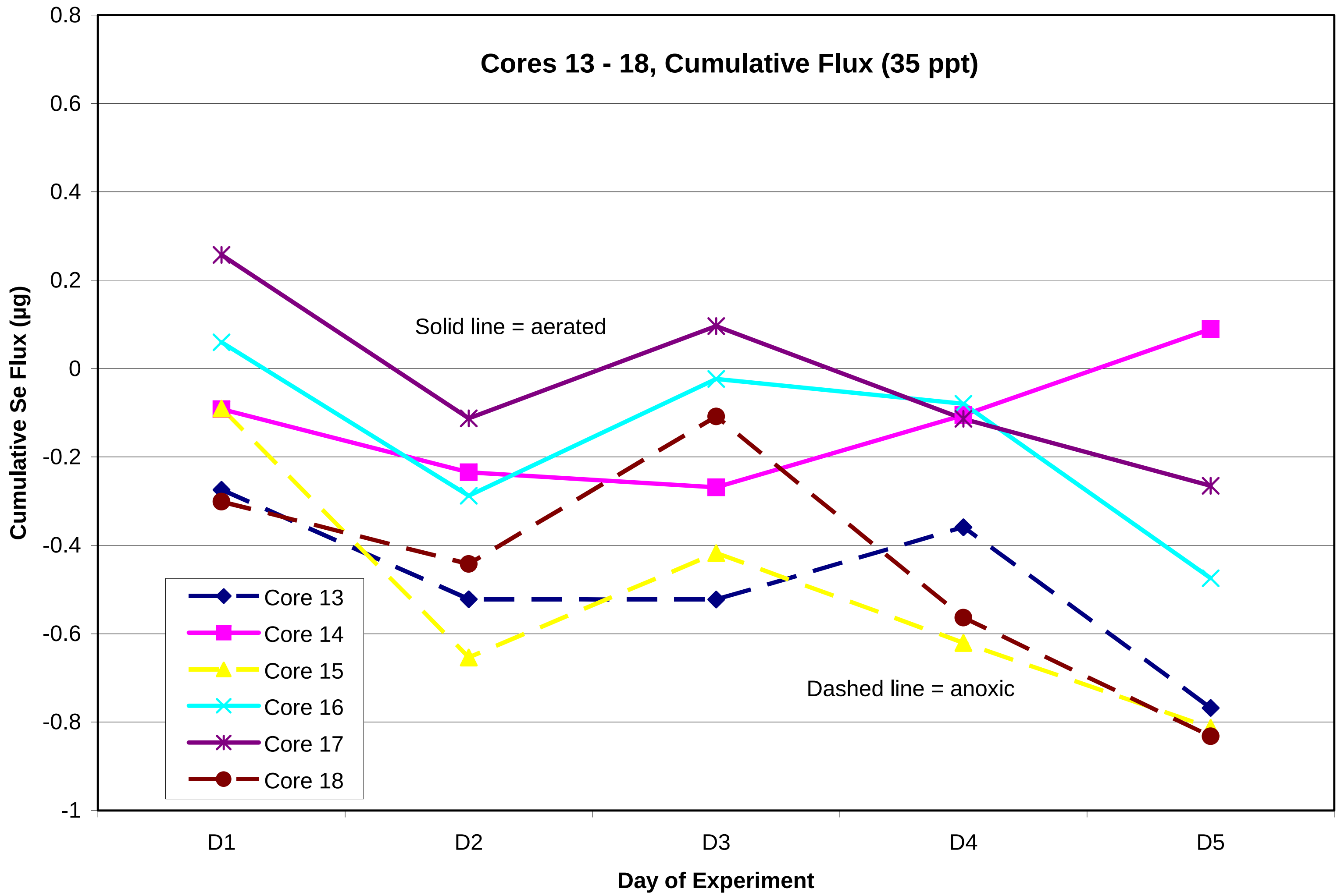

Figure 2c
Cumulative Selenium Flux over the 5-day Experiment Shown as Load/Core from the Sediment (+ Values) or into the Sediment (- Values) for 35 ppt Overlying Water. Aerated Cores Are Solid Lines, Anoxic Cores Are Dashed Lines.

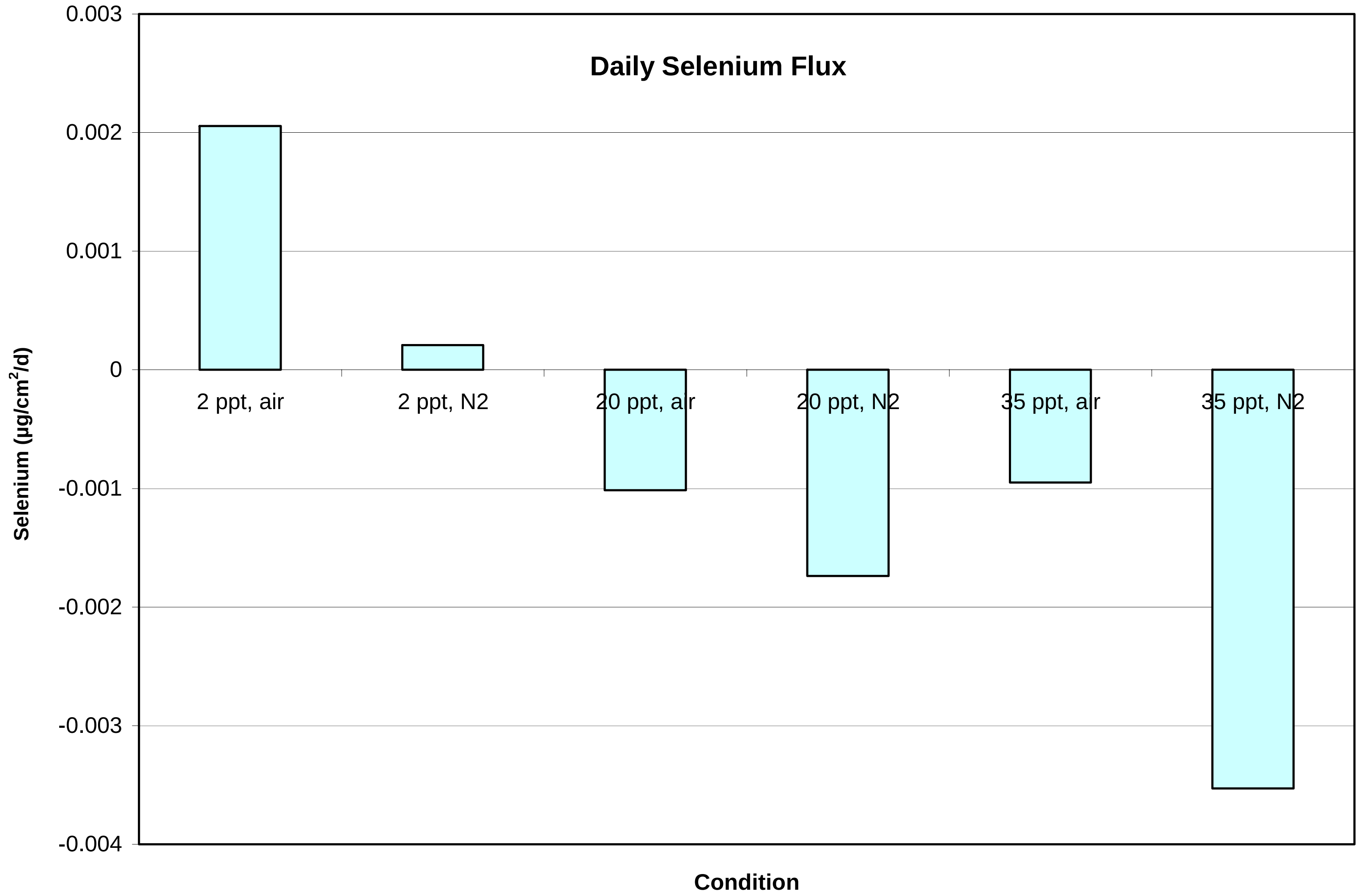

Figure 3
Total Selenium Flux over Five Days, Adjusted as Load from (+ Values) or into (- Values) the Sediments on a Daily Basis per Area of Sediment Surface.