Direct, In-Situ Measurement of Diffusive Metal Fluxes from the Sediments of Sinclair and Dyes Inlet, Washington

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Introduction

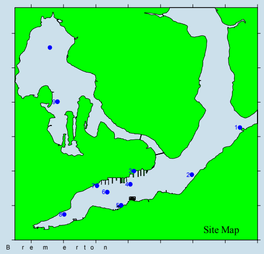
Site characterization studies, NPDES monitoring, and recent regulatory listings all point to sediments as a potentially important repository for contamination in Sinclair and Dyes Inlets, Washington (Katz et al., 1999). It is also recognized that the subsequent remobilization of these contaminants represents a potential source to the Inlet that may be important in overall contaminant budgets and development of Total Mass Daily Loads (TMDLs). The remobilization may also be an important indicator of exposure in areas where the initial discharge material is substantially particle-bound, as may be the case for dry-dock discharges and stormwater flows.

To address these issues, we made direct, in-situ measurements of contaminant remobilization rates using the Navy-developed Benthic Flux Sampling Device (BFSD). Ten sites were examined in the Sinclair/Dyes Inlet system. Measurement sites were chosen to represent a range of bulk contaminant loadings and geochemical conditions. Target analytes including metals and nutrients were selected based on previous monitoring and site characterization data. Flux rates were found to show considerable range with highest rates for Zinc, Nickel, and Copper, and generally lower rates for Lead, Cadmium and Silver. The range of flux rates is consistent with rates measure in other similar coastal environments.

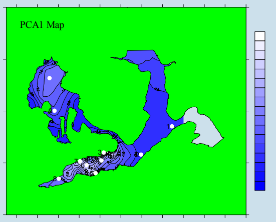
In an effort to extend the point measurements of flux to the inlet system in general, the measured benthic fluxes at the ten stations were correlated to metal concentrations, percent TOC, and percent fines. Good correlations between flux rates and bulk sediment parameters were found for Cadmium, Copper, Nickel and Zinc. Where possible, the resulting correlations were then used to extrapolate fluxes based on a broader database of bulk sediment data from SEDQUAL (Sediment Quality Information System). The resulting flux maps were then incorporated on an inlet-wide basis to provide mass loading terms for the TMDL study.

Methods

Analytes: Analytes for the flux study were selected to address issues of conventional and toxic contaminant loadings. Conventional water quality analytes were assessed to address issues of nutrient loading and oxygen demand. These analytes were selected based on historical observations of algal blooms and hypoxia in Sinclair Inlet. Toxic contaminants for the study were selected based on previous listing on the 303d list, or other indications of possible ecological risk. Toxic contaminants were limited to metals due to current limitations of the flux chambers. Results for nutrients are not included in this presentation.



Sites: The overall study region includes Sinclair Inlet, Dyes Inlet, Port Orchard Passage, and Rich Passage (see figure at right). This region was chosen to correspond to the model domain for the TMDL study. Field measurement sites in the region were chosen to represent a range of bulk contaminant loadings and geochemical conditions. A number of historical studies were reviewed to develop a sense for the distribution of TOC, grain size, and metals in sediments. TOC should serve as an indicator of organic matter loading, with related variations in oxygen demand and nutrient flux. Metals distributions provide a general indication of the range of contaminant mass available for remobilization. TOC and grain size distribution provide a general geochemical indicator of the binding capacity of the sediments, and serve as potential controls on remobilization. Distributional maps were developed from the historical data (not shown).



The historical data was further analyzed using principal component analysis (PCA) to evaluate general and localized trends in metals and TOC. PCA provides a method for evaluating the relative contribution of multiple parameters to the overall variance of a multidimensional data set. Sufficient historical multi-parameter data was available for seven metals and TOC for 208 measurements (some historical measurement sites included multiple sample events at the same site). Results from the PCA are shown in the tables below. The first principal component (pca1) explains about 45% of the data variance is relatively equally weighted across all metals and TOC, and reflects the general regional covariation between metals and for metals and TOC. Pca2 through pca6 each explain ~6-12% of the variance and indicate variations from the general trend. Pca2 indicates co-enrichment in Cd, Hg and Ag, pca3 indicates co-enrichment of Pb and Hg, pca4 indicates enrichment of TOC, pca5 indicates co-enrichment of As and Ag, and pca6 indicates enrichment of Cu. The spatial relationship of the station locations and the PCA scores for pca1 are shown spatially in the figure above.

The final station locations selected based on this analysis are shown in the upper figure. Station 1 and 2 were selected as characteristic of the Port Orchard/Rich Passage region, an area of low metals and TOC with correspondingly low pca1 scores. Stations 3, 5 and 7 were chosen to represent potential source areas in Sinclair Inlet with high metals and high pca1 scores. Stations 4, 6 and 8 were chosen to be representative of central Sinclair Inlet with moderate metals levels and pca1 scores, and moderate to high TOC levels. Stations 9 and 10 were selected to represent Dyes Inlet, with station 9 reflecting moderate metals levels, and station 10 characterized by moderate to high metals and TOC.

Flux Sampling: The flux sampling was carried out using two Navy developed flux chambers, BFSD1 and BFSD2 (see photos at right; Chadwick et al., 1994). The chambers are similar in construction and function, but vary slightly in operation. In general, operations for BFSDs were in accordance with standard operating procedures (SOPs) documented in Chadwick and Stanley, 1993, and subsequent modifications adopted for CALEPA and described in Hampton and Chadwick, 2000. Flux sampling was conducted at the ten stations described above. At each site, a flux chamber was be deployed for a period of ~3 days during which a series of 10-12 samples were collected. At the end of the period, the chamber were retrieved, the samples processed and delivered to the analysis lab. During the field deployments is was determined that there was no adequate sediment substrate present at site 1. This site was dropped, and a replicate deployment at site 4 was substituted.

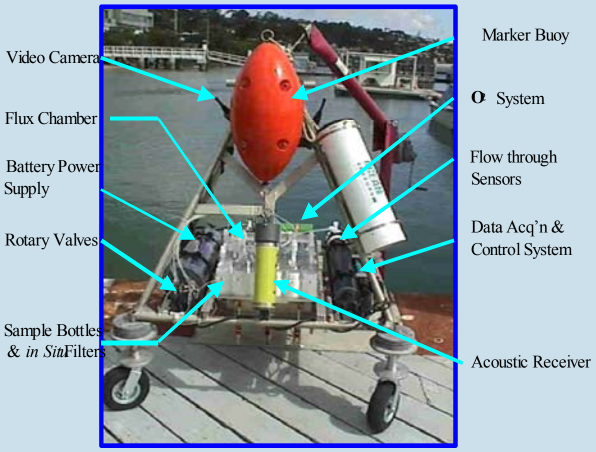
Empirical Flux Model: In attempt to extrapolate the results from our ten measurement stations to the TMDL model domain, we adopted a simple, multiple linear regression model (e.g. Zar, 1984). The independent variables for the model including bulk sediment concentration, TOC, % fines, iron and aluminum, were chosen from parameters that are commonly measured in monitoring programs, and are available over a large range of the domain. They were also chosen because they are commonly accepted proxies for contamination levels, binding substrate, or background mineralogy. The regression model for the benthic flux, Y_{bf} (ug/m^2/day), and the sediment parameters can be expressed by the following equation:

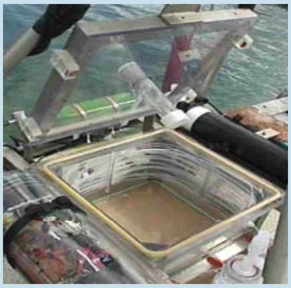
$$Y_{bf}=A_1X_1+A_2X_2+A_3X_3+A_4X_4+A_5X_5+A_6$$

Principal Component	PCA Coefficients TOC	As	Cd	Cu	Pb	Hg	Ag	Zn	Variance Explained
pca1	0.334	0.278	0.420	0.360	0.392	0.369	0.355	0.299	45.49%
pca2	-0.003	-0.599	0.291	-0.434	-0.071	0.264	0.514	-0.169	12.57%
pca3	0.061	0.051	-0.370	0.132	0.341	0.458	-0.044	-0.715	10.70%
pca4	0.628	0.112	0.131	0.178	-0.425	-0.374	0.203	-0.428	9.82%
pca5	-0.491	0.643	0.038	-0.168	-0.258	0.044	0.468	-0.171	8.58%
pca6	-0.473	-0.349	0.135	0.736	-0.035	-0.193	0.180	-0.151	6.05%
pca7	-0.039	0.045	0.062	-0.228	0.690	-0.633	0.192	-0.162	3.87%
pca8	-0.152	0.109	0.749	-0.104	0.013	0.067	-0.528	-0.331	2.91%

Station	TOC (%)	As (mg/kg)	Cd (mg/kg)	Cu (mg/kg)	Pb (mg/kg)	Hg (mg/kg)	Ag (mg/kg)	Zn (mg/kg)	pca1 score
1	1.8	11	0.61	140	55	0.47	0.72	120	-1.44
2	1	2.7	0.7	8	11.8	0.1	0.4	36.1	-2.40
3	2.82	85.6	2.7	1410	231	1.1	5.5	996	6.27
4	2.89	13.6	2.7	109	101	0.93	5.3	166	1.12
5	3.1	16.8	2.7	1240	164	1	2.1	654	3.57
6	2.51	12.9	5.3	127	84.8	1	10.6	157	2.93
7	2.12	67	1.1	807	233	1.28	2.3	873	3.31
8		19.8	4.3	138	94.6	1	3	201	na
9	2.3	9.4	1.2	46.1	68.3	0.51	1.1	128	-0.94
10	3.2	18.8	1.41	113	57.4	0.659	0.85	143	-0.40

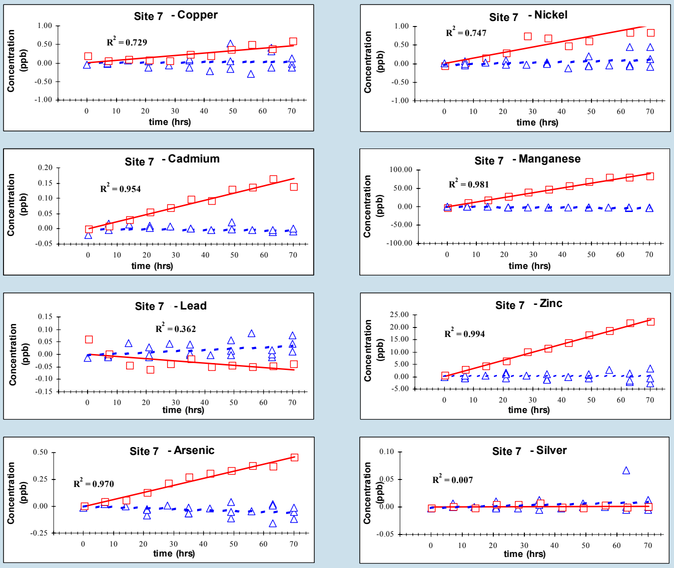
Where X_1 represents bulk sediment metal concentration (ug/g DW), X_2, percent fines, X_3 percent TOC, X_4 iron concentration, X_5 aluminum concentration. Regression coefficients A_1-A_6 are obtained by enforcing the least-square error requirement. After the regression models were developed for each target metal, data from the SEDQUAL (SEDiment QUALity Information System) database was used to extrapolate the benthic flux results to the greater Sinclair and Dyes Inlets region.





Results

Flux Measurements: Flux rates were measured successfully from ten deployments for six metals including As, Cd, Cu, Ni, Pb, and Zn. Results for Mn, dissolved oxygen, and nutrients were also obtained but are not presented here. A broad range of metal fluxes were observed across the ten stations with largest fluxes for Zn and lowest fluxes for Cd and Pb. Among the ten stations, highest fluxes were generally observed at stations 3 (see below) and 7, and lowest fluxes at station 2. Fluxes of metals observed at these sites are consistent with flux rates observed in other areas including San Diego Bay (Leather et al., 1995), Pearl Harbor (Apitz and Kirtay, 1999), and San Francisco Bay (Leather et al., 1999).



Typical time series results from the BFSD deployment at station 7 are shown in the figure below left. Several metals show strong increasing linear trends that are characteristic of metal mobility and flux to the overlying water (e.g. Cu, Cd, Mn, Ni, As, Zn). These fluxes (shown in red) are clearly distinctive from chamber blanks (shown in blue). Flux results from all of the BFSD deployments are summarized in the table at right. Shaded cells indicate fluxes that were statistically significant compared to blanks. Although the remaining results cannot be distinguished statistically from a no-flux condition (blank), they were retained in the subsequent empirical model.

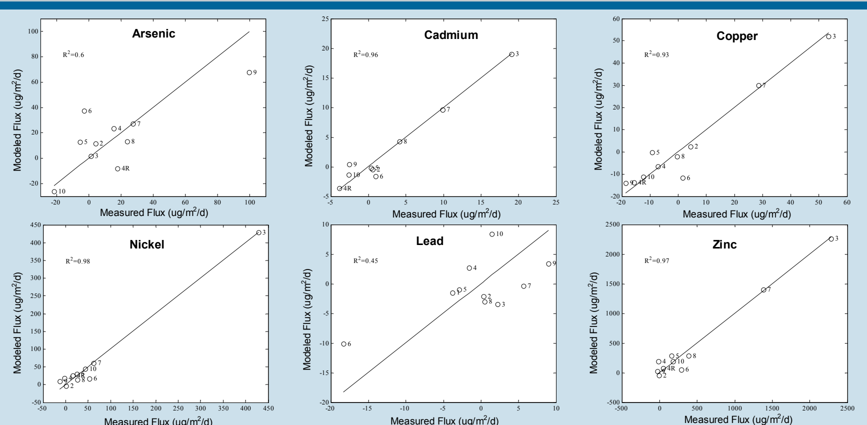
Station	Flux Rate ($ug/m^2/d$)					
	As	Cd	Cu	Ni	Pb	Zn
2	4.41	0.570	4.41	0.722	8.98	-4.25
3	1.34	19.1	53.5	429	0.327	2284
4	15.5	NA	-7.16	-1.98	0.520	-12.5
4R	17.8	-3.84	-15.7	16.2	-2.86	47.9
5	-5.30	0.385	-9.19	24.9	2.24	157
6	-2.70	1.01	1.64	52.7	5.66	293
7	27.5	9.89	28.7	62.6	-3.76	1382
8	24.0	4.15	-0.301	26.7	-18.3	386
9	99.7	-2.57	-18.5	-12.2	-1.59	-25.5
10	-21.5	-2.62	-12.4	43.51	1.49	184

Sediment Parameters: Measurements for independent model variables are shown in the table below. As with the flux rates, these bulk sediment characteristics showed a broad range of concentrations across the ten stations. For example, sediment concentrations of metals varied by over an order of magnitude for many parameters. Highest levels of several sediment metals including As, Cu, Ni, Pb and Zn were observed at stations 3 and 7. Lowest sediment metals levels were generally found at station 2. Thus a general consistency between bulk sediment metal concentration and flux rates was observed. However, note also that a broad range of concentrations were also present for important binding and mineralogical constituents. For example, TOC levels ranged from 0.22 % at station 2, to 5.36% at station 8. Thus it is expected that bulk sediment concentration alone will not be a good predictor of metal mobility. Taken together, these results suggest that the measurement program was successful in capturing a significant portion of the potential variability present throughout the region.

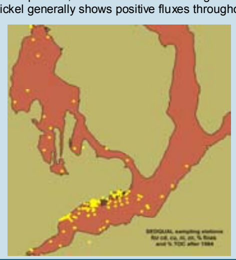
Station	Independent Variables									
	As ug/g	Cd ug/g	Cu ug/g	Ni ug/g	Pb ug/g	Zn ug/g	Fines %	TOC %	Fe ug/g	Al ug/g
2	4.03	0.171	12.8	22.4	13.9	51.2	5.56	0.22	24800	81100
3	81.5	2.03	815	285	238	1390	45.8	5.85	63000	59500
4	14.9	0.692	108	46.9	71.9	160	80.45	3.78	41300	82500
4R	15.5	0.738	113	48.4	87.8	170	92.79	3.1	43900	86500
5	16.3	3.12	219	55.2	83.5	270	96.345	4.245	45200	84200
6	15.5	0.793	132	49.2	91	174	97.15	3.36	42600	81900
7	260	0.497	545.5	39.85	334.5	1280	19.83	1.28	40650	51100
8	15.7	2.02	127	52.1	75.7	170	96.61	5.36	43900	86500
9	11.7	0.998	67.8	46.4	56.2	140	85.51	3.16	39100	78200
10	8.32	0.732	35.2	38	25.4	91.1	28.79	1.13	37700	81100

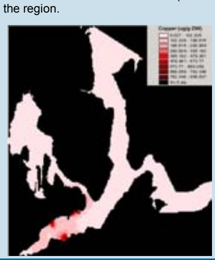
Regression Modeling: Results from the multiple linear regression models are shown in the plots at right. Of the six metals, four showed good results for the regression modeling including cadmium (R^2 = 0.96), copper (0.93), nickel (0.98), and zinc (0.97). For arsenic and lead, the regression models were not so successful with typical R^2<0.6. While the regression for nickel is dominated by the results from station 3, it is reassuring that for the other metals there are additional intermediate points that substantiate the relationships. Regression coefficients (shown below) give some insight into the role of various parameters in the correlation, although this must be interpreted with care. In general, it can be seen that with the exception of cadmium, all of the metals with strong regressions have positive A1 coefficients, suggesting that flux rates to generally increase with increasing bulk concentration. Stepwise regression analysis (not shown here) confirms this finding. The cadmium flux appears to be more closely related to the TOC concentration. This again was confirmed by stepwise regression analysis, which also suggested that % fines may play a role.

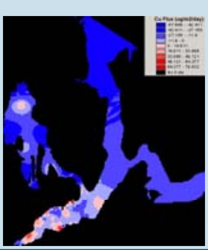
Parameter	Regression Model Coefficients					
	As	Cd	Cu	Ni	Pb	Zn
A_1 (Bulk)	-0.491	-0.548	0.103	1.34	-0.0904	0.8584
A_2 (Fines)	1.202	-0.12	-0.238	-0.680	0.0692	-8.02
A_3 (TOC)	7.53	4.02	4.97	-6.21	-4.66	104.21
A_4 (Fe)	-0.0055	-0.0001	-0.0012	0.0038	0.0007	0.0226
A_5 (Al)	-0.0068	-0.0003	0.0004	0.0001	-0.0006	-0.0014
A_6 (Const)	688.8	27.23	-0.148	-128.2	35.56	-521.5
R^2	0.60	0.96	0.93	0.98	0.45	0.97



Flux Mapping: The first figure here (below left) shows the sampling stations for cadmium, copper, nickel, zinc, iron, aluminum, percent fines, and percent TOC from the SEDQUAL database (year > 1984). Note that majority of the SEDQUAL sampling stations reside close to the Naval Shipyard in Sinclair Inlet. Also, please note the lack of sampling stations at Rich Passage and Port Orchard Passage result in low confidence in the contours in these particular areas. The second figure (below middle) shows the interpolated grid for copper concentration in the sediments based on SEDQUAL data (SEDQUAL, 2002). The figure reveals that higher copper levels are generally confined to Sinclair Inlet, and are concentrated around shipyard, marina, and outfall areas. The final figure (below right) shows the predicted benthic flux of copper interpolated across the entire region based on the regression model described above. ArcView GIS was utilized to create interpolations based on the IDW technique using the nearest 12 points. The blue indicates negative benthic flux meaning the flux is in, thus the toxicant is going into the sediment. Inversely, the red indicates that the flux is positive, and the toxicant is fluxing out of the sediment. Cadmium and zinc (not shown) have similar patterns to copper, while nickel generally shows positive fluxes throughout the region.







Summary and Conclusions

In this study, we attempted to estimate the loading of metals from benthic fluxes to the Sinclair/Dyes Inlet system using a combination of historical sediment data, recent flux chamber measurements, and empirical regression modeling. The field measurement program was successful in capturing a range of conditions across the Inlet system for both fluxes and bulk sediment properties. The regression analysis led to good predictions for cadmium, copper, nickel and zinc, but poor results for lead and arsenic. For most metals it appears that the dominant controlling factor was the bulk sediment concentration, while other sediment characteristics contributed but to a lesser degree. The exception to this was for cadmium where TOC and fines appear to be dominant. Application of the empirical model to the larger historical data set from SEDQUAL allowed interpolation of the flux measurements to the entire Inlet system. In the future, these estimates will be incorporated into the TMDL model that is being developed for the region.

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