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Feature

Historical Inputs and Natural Recovery Rates for Heavy Metals and Organic Biomarkers in Puget Sound during the 20th Century

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Anthropogenic burdens recorded in sediment reveal a case for recalculating natural recovery rates. Such new models would forecast the continued increase in nonpoint source inputs in the 21st century.

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Eric Crecelius (left) and Jill Brandenberger process a 10 foot sediment core in Puget Sound, with Mount Rainier looming in the background.

Sediment cores were collected in central Puget Sound from one location near Seattle and one near Tacoma during three coring studies conducted in 1982, 1991, and 2005. The core reconstructions clearly show increased inputs of inorganic (Pb, Cu, and As) and organic markers (lignin and soil biomarkers) during timeframes relevant to human activity and environmental regulations. The three coring studies provided the opportunity to calculate a simplistic natural recovery rate for the 20th century using a regression of surface sediment chemistry versus elapsed time. Sediment concentrations of Pb and Cu were estimated to recover back to preindustrial conditions ca. 2020–2030. However, this method may not represent the 21st century with increased urbanization in Puget Sound and the subsequent rise in the importance of nonpoint source inputs. In fact, nonlinear trends in the 2005 cores suggest a slowing of the 20th century recovery rate. While As has shown near complete recovery due to removal of the point source, 21st century recovery rates for Pb and Cu project recovery around 2030–2060.

Retrospective view of environmental regulations

Environmental regulations passed during the mid-20th century, such as the Clean Water Act (CWA), aimed to protect ecological health by addressing point and nonpoint source discharges. Measuring the effectiveness of environmental regulations is extremely complex in dynamic coastal environments. This complexity stems from the very nature surrounding the evaluation of ecological health where intersections occur between anthropogenic stressors and natural physical, chemical, and biological processes. One method for evaluating the effectiveness of these regulations is by reconstructing the historical inputs of contaminants back to preindustrial conditions. In the case of metals, this method provides a means of separating anthropogenic from natural inputs and allows the calculation of the anthropogenic burden and its changes over time. The use of sediment cores to reconstruct geochronologies reflecting watershed-integrated loads of metal and organic contaminants is well documented (e.g., *1–6*). These studies all show similar trends with marked increases of metals during urbanization in the watershed, followed by decreasing concentrations around the middle of the 20th century as environmental regulations begin reducing point source inputs. These studies, along with the Puget Sound studies, demonstrate that environmental regulations have been effective at reducing the point sources of contaminants with subsequently overall positive effects on water quality. However, with rising coastal zone development and the increasing relative importance of nonpoint sources, one might ask the question, "How effective are the current environmental regulations at controlling 21st century nonpoint source discharges?"

The current regulatory development and implementation process within the CWA has grown less and less effective with the increasing dominance of nonpoint sources, which are far more difficult to regulate as, by definition, they are not associated with a specific process or responsible party. This need to develop a new model for regulatory controls has been recognized by the U.S. Environmental Protection Agency (USEPA) (*7*), but progress toward 21st century regulations has been outpaced by population growth in many coastal areas, such as Puget Sound.

In Puget Sound, population growth trends for three coastal counties (King, Pierce, and Kitsap counties) have been linear

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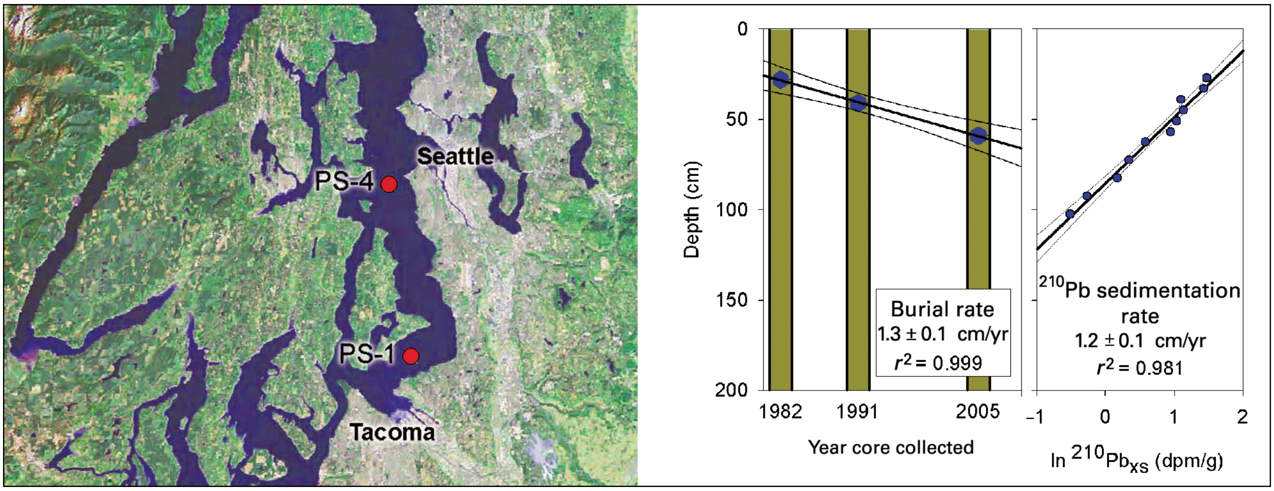

FIGURE 1. Coring locations PS-1 and PS-4 in central Puget Sound are located on the map (left). Sedimentation rates at PS-1 are calculated by burial rate as linear regression of peak in total Pb, with 95% confidence intervals, for cores collected in 1982, 1991, and 2005 (right: year core collected); and ^{210}Pb as linear regression, with 95% confidence intervals, of natural log excess ^{210}Pb activity versus accumulation in 2005 (right: ^{210}Pb sedimentation rate).

for the last 50 years (*8*). A majority of this growth has occurred outside of designated urban growth areas, which represents the new pattern of human settlement referred to as "sprawl" (*9*). There are national trends in this type of development with more than 95% of U.S. population growth occurring as "sprawl", which requires a higher dependency on automobiles (*10*). In 2005, the USEPA determined that urban runoff was the leading source of pollutants causing water quality impairment in sensitive coastal systems across the nation (*11*). Indeed, urban centers are substantial pollution hot spots (*12*), where the combination of increased impervious surface areas and hydrodynamic pulse events amplifies the episodic transfer of priority pollutants to aquatic systems. Elevated levels of Pb and Cu in urban runoff are typically derived from a mixture of sources including atmospheric deposition (regional and global), automobiles, highways, and other impervious surfaces (*11*). This type of development in coastal areas has been linked to water quality declines (*13*), shoreline modifications (*14*), and habitat destruction (*15*).

Geochronology for Puget Sound

To evaluate impacts of urbanization in Puget Sound, Bloom and Crecelius (*3*) published the first historical reconstructions for Pb, Cu, Ag, Hg, and Cd concentrations from sediment cores collected in 1982. Sediment cores were collected using a stainless steel Kasten corer with 3-m-long core barrels and cross-sectional area of 225 cm^2, which minimizes core shortening (*3*). In 1991, sediment cores were collected using the same techniques and locations near Seattle (PS-4) and Tacoma (PS-1; Figure 1). In 2005, a third coring study was conducted at these sites using the same techniques, which allowed a comparative analysis of surface sediment chemistry and metal profiles over a time span of two decades. The geochronologies for these studies were independently established based on radiometric dating (*3, 4*). All three studies suggest that sediment deposition and ^{210}Pb fluxes were relatively constant over time with a surface sediment mixing depth of 10−20 cm. Sedimentation (cm/y) and accumulation rates (g/cm^2/y) were estimated using steady-state ^{210}Pb dating techniques (*16, 17*).

Many studies have incorporated these methods for establishing geochronologies and rates of natural recovery. However, the application of these methods and other radiometric sedimentation models has recently come under criticism for oversimplification or inappropriate assumptions (*18*). For example, Bloom and Crecelius (*3*) recognized their method was simplistic and potentially underestimated the effect of mixing on the ^{210}Pb profiles, which would lead to overestimating sediment accumulation rates. Smith (*18*) proposed ^{210}Pb geochronology be validated using at least one independent tracer that separately provides an unambiguous time-constrained stratigraphic horizon. The availability of three separate coring studies at the same locations, spanning 23 years, provided an opportunity to identify such an *in situ* independent tracer incorporating all diagenetic processes. For example, at the PS-1 coring location the burial of an observed peak in total Pb served as an ideal independent stratigraphic tracer (Figure 1). In the 1982 core, the highest total Pb concentration was in the 21−34 cm core segment (*3*), in 1991 this peak was at 38−44 cm (*4*), and in 2005 it was at 58−60 cm. A regression of the depth of the peak-Pb horizon versus elapsed time indicates that cleaner sediments are burying historically more contaminated sediments at a linear rate of approximately 1.3 ± 0.1 cm/y. This value is comparable to the one obtained through radiometric dating in 2005 (1.2 ± 0.1 cm/y; Figure 1). Applying the same approach to the PS-4 site provides a burial rate of 2.8 ± 0.5 cm/y and sedimentation rate of 2.1 ± 0.3 cm/y. These results agree with the previous studies and confirm that the total Pb profiles were not significantly altered by diagenetic processes.

Point-source pollution control

The Puget Sound cores provide a historical record of watershed-integrated metal and organic biomarker inputs. Features observed within this relatively high-resolution record can be directly linked to specific events within the Puget Sound watershed. For example, the Pb profiles from the three coring studies show the first accumulation of anthropogenic Pb around 1890 when metal smelting began near Tacoma (Figure 2). The anthropogenic Pb concentrations continue to increase during the early 1900s and the first peak occurs during World War I (WWI; 1914−1918) when significant industrialization began in central Puget Sound. The Pb concentrations then show a decrease during the Great Depression (1929) followed by a second increase during WWII (1930s−1945), a peak in the 1960s, and finally significant decreasing trends since the implementation of the first environmental regulations.

Total As concentrations are also linked to specific point sources, such as As emissions from a metal smelter near

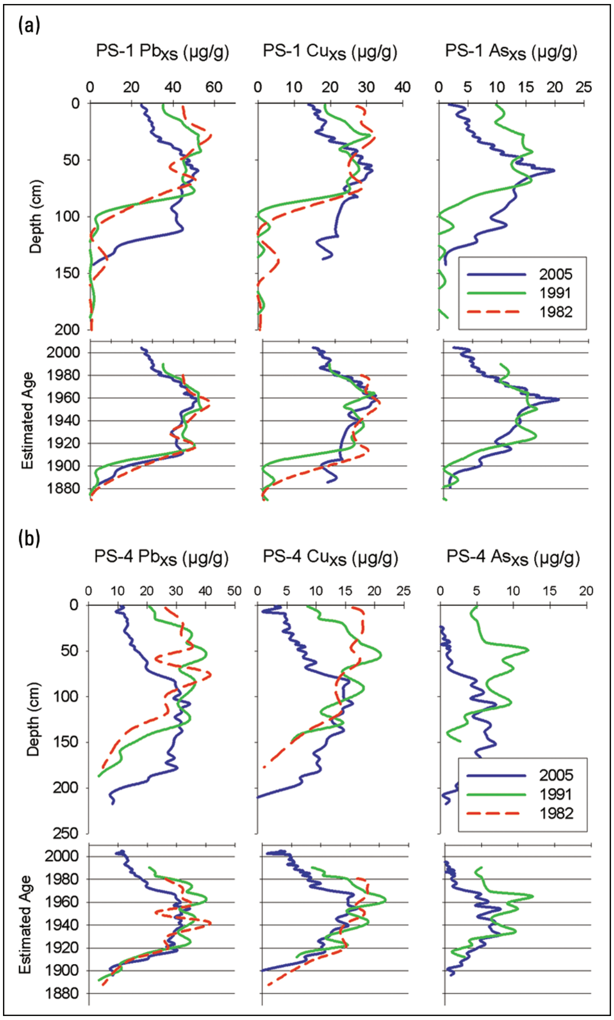

FIGURE 2. Sediment core profiles for excess Pb, Cu, and As at (a) PS-1 and (b) PS-4. Cores were collected in 1982, 1991, and 2005.

Tacoma that operated from 1890 to the 1980s (*19*). The As concentrations increase above background beginning ca. 1900, peak ca. 1960, and decrease significantly following the smelter closing in 1986 (Figure 2). It is tempting to use such rates of decrease to calculate absolute natural recoveries of sediment contamination. However, the rate of natural recovery can only be defined relative to the native sediment composition, which is influenced by the dominant geologic formation of the drainage basins. The PS-1 core extends back to preindustrial sediment used to define the background concentrations of Pb = 10.7 ± 1.1 μg/g, Cu = 34.3 ± 2.1 μg/g, and As = 8.57 ± 1.5 μg/g in Puget Sound. The background was subtracted from the total metal concentrations to determine the excess or anthropogenic fraction. Figure 2 illustrates the excess Pb, Cu, and As profiles for each of the three coring studies (except As in 1982). The excess metal concentrations were plotted against down-core depth and then normalized to estimated age of deposition (Figure 2). The core profiles show that, historically, sediments near the more industrialized area of Tacoma (PS-1) received higher inputs of anthropogenically derived metals than the predominantly urban Seattle area (PS-4). In fact, the depositional area near Seattle contains no anthropogenic As, whereas around 15% (3 μg/g) of anthropogenic As remains in the mixed layer of PS-1. Thus, the geochronologies obtained from metal concentrations at two different locations clearly demonstrate changes in anthropogenic inputs to Puget Sound during urbanization over the last 100 years.

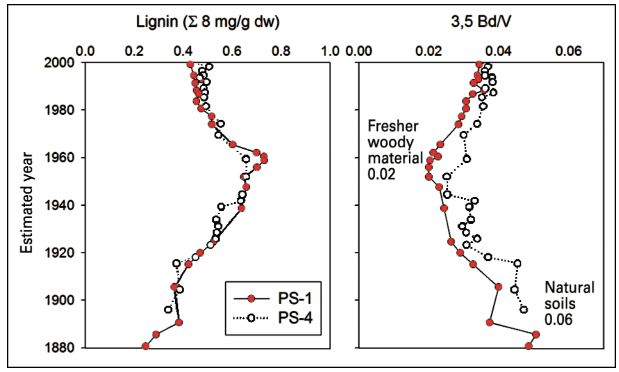

FIGURE 3. Lignin concentrations (Σ 8) and soil biomarker ratios (3,5 Bd/V) for the 2005 cores.

Organic biomarkers that trace land-cover changes by recording marked shifts in the source of terrestrial organic matter (TOM) are also used to reconstruct impacts of urbanization in central Puget Sound watersheds. This approach has been used successfully to characterize erosional inputs of soil organic matter (SOM) or plant material inputs derived from industrial activities (i.e., forestry, pulp and paper mills, etc.) (*20*–*22*). Lignin, an exclusive molecular constituent of vascular plants, and humic-derived biomarkers thus help trace not only the unambiguous increase in TOM (*20*), but also changes in the quality of those inputs (i.e., humified SOM vs fresh woody materials) (*20, 21*). The 2005 core profiles for lignin (reported as the sum of eight oxidation products = Σ 8) and soil biomarker (reported as the ratio of 3,5 dihydroxybenzoic acid to vanillyl phenols = 3,5 Bd/V) were used to detect significant shifts in the load of SOM to the receiving waters (*20, 21, 23*). The lignin profiles show a significant departure from preindustrial signatures around the 1900s, which marked the start of significant logging in the Puget Sound lowlands (*24*). Similar to the metals, lignin inputs peak from 1940–1960 and confirm that the increase in urbanization and land clearing transported greater amounts of TOM to Puget Sound. The active forestry and pulp and paper industry in the region has significantly contributed to the transfer of lignin to the basins. Parallel to this increase in TOM inputs, strong shifts in 3,5 Bd/V ratios from natural soils (0.06) to fresher woody material (0.02) were observed (Figure 3). The excellent agreement between the two profiles provides an independent validation of the radiometric dating. Moreover, the recovery of both biomarkers post-1960s further points to the influence of environmental regulations on both the pulp and paper industry and land management in the watershed.

20th versus 21st century natural recovery rates

The agreement among the three coring studies is remarkable and confirms that simplistic surface sediment recovery rates, which inherently incorporate sediment mixing and diagenesis, can be estimated in a site-specific manner. The 20th century natural recovery rates for the two coring locations were calculated using the average concentration of the surface mixed layer (upper 10 cm) for each coring study relative to elapsed time between corings (Figure 4). Recovery rates calculated for both the 0–10 and 0–20 cm segments were within the margin of error for each rate. Therefore, recovery rates are calculated using the 0–10 cm segments to remain consistent with sediment monitoring studies. Figure 4a shows a linear decrease in the excess metal concentrations in surface sediment over the course of two decades. At this rate, metal concentrations in the surface sediment of central Puget Sound are estimated to recover back to preindustrial concentrations ca. 2035 for Pb, 2030 for Cu, and 2010 for As at PS-1, and 2025 for Pb and 2010 for Cu at PS-4.

for determining a separate recovery rate for the 21st century. If the rate of human changes in the last two decades represents those anticipated for the future, then recovery estimates should be revised. The 21st century recovery rates were calculated using the linear regression and 95% confidence interval for data from 1988 through 2005 (Figure 4b). Using the new 21st century rates, sediments near Tacoma (PS-1) are predicted to reach preindustrial concentrations ca. 2070 ± 15 for Pb and 2050 ± 28 for Cu, whereas sediments near Seattle (PS-4) are predicted to recover by 2050 ± 20 for Pb and 2020 ± 10 for Cu. The excess As was primarily associated with a point source that was shut down in 1986. Thus, recovery estimates for As at PS-1 (2012) were the same using both 20th and 21st century recovery rates (PS-4 has already recovered for As).

With this approach, the recovery rates of TOM/SOM biomarkers estimate sediment will reach preindustrial signatures around 2073 ± 2 for TOM and 2116 ± 11 for SOM at PS-1 and PS-4, respectively. The longer recovery time obtained from organic tracers illustrates the diffusive inputs of SOM throughout the entire watershed and supports the concept of a recent shift in metal recoveries toward a slower rate. The projected recovery rate from soil signatures (3,5 Bd/V) may be an overestimate as fine soil particulate matter (enriched in 3,5 Bd) will always be masked by erosional inputs of surface SOM (depleted in 3,5 Bd) in watersheds with active land clearing.

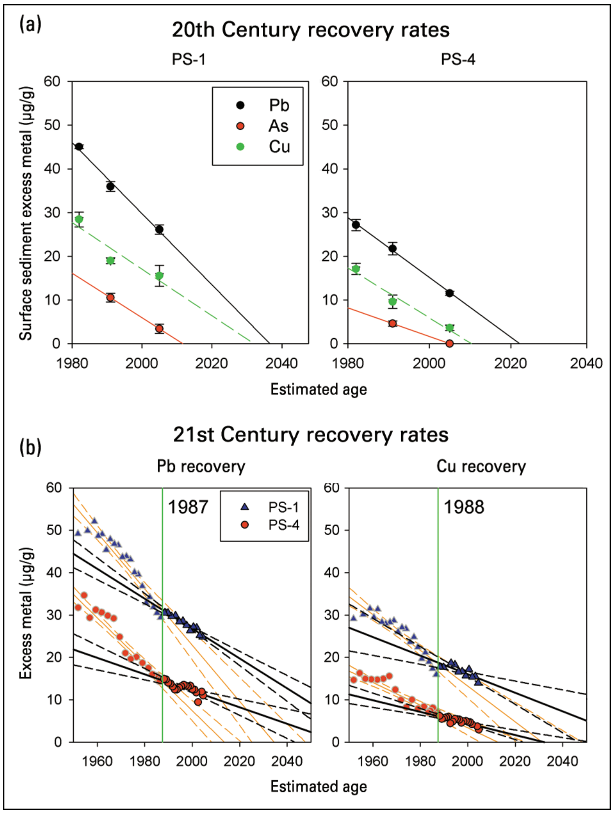

FIGURE 4. (a) 20th century recovery rates. Estimated natural recovery determined from the linear regression of the average excess metal concentration for the upper 10 cm of both the PS-1 and PS-4 cores, from the three coring studies in 1982, 1991, and 2005. (b) 21st century recovery rates. The green line indicates linearity breaks for the 2005 cores. The regressions and 95% confidence intervals are shown for the 20th century (orange) and predicted for the 21st century (black) for excess Pb and Cu.

There are many sources of potential error in these simplistic recovery estimates. The most quantifiable is the error associated with sediment mixing and estimated age of deposition. The surface segment is assigned the date of core collection; therefore, the error is derived only from the analytical measurements and the linear fit. For this linear approach to be used to estimate long-range sediment recovery, several assumptions must be met: (1) changes in metal sources or reductions will vary proportionally or remain relatively constant into the 21st century and (2) sediment supply and mixing processes remain constant. The geochronology data indicate that the second assumption has not been violated for central Puget Sound coring locations, as the overall sediment flux has remained relatively constant. However, the first assumption will inevitably be violated with the rise in coastal growth and development. The increase in populations and emergence of more “sprawl”-type development in coastal zones will tend to shift the sources of metal pollutants from point sources to more diffuse and complex sources.

To test whether the first assumption has already been violated in the most recent sediments, the 2005 core was evaluated for nonlinear trends in the observed decreases of excess Pb and Cu concentrations since the 1960s. Figure 4b shows the segmented regression of the 2005 PS-1 and PS-4 cores for Pb and Cu. The regression analysis indicates a significant break in the linearity occurring around the late 1980s [green lines indicate year for Pb ($p \le 0.01$) and Cu ($p = 0.03$)]. This suggests that the rate of sediment recovery in the last two decades has slowed, which provided the basis

Future perspectives

These three coring studies provide empirical evidence that environmental regulations have had a positive impact on the overall water quality of Puget Sound with respect to select metals and organic matter. Regulatory controls on point sources, enacted since the 1970s, resulted in a significant reduction in the anthropogenic burden recorded in sediments of Puget Sound, which represent watershed-scale conditions. In fact, the excess profiles for As are the perfect example of point source controls coupled with natural recovery. After removal of the primary source in 1986, sediments in central Puget Sound are back to preindustrial concentrations near Seattle and contain only a small excess near Tacoma. The As was used to test the sensitivity of our recovery rates and confirmed that projected recovery dates were the same using both 20th and 21st century rates. However, the rate of recovery for Pb and Cu has decreased since around 1988. This suggests that point source controls enacted in the 20th century significantly reduced the anthropogenic burden for these metals, but diffuse sources may impede the continued progress of recovery. Recovery projections using the 20th century rates estimate achieving preindustrial concentrations ca. 2020–2030. Revising these estimates for 21st century conditions gives a projected recovery range of 2030–2060. These results confirm that new approaches to regulating nonpoint sources are necessary to continue natural recovery and priorities should be set to identify nonpoint sources both regionally and globally, create strategies to reduce or eliminate these sources, and unify monitoring programs to invest in coordinated efforts to achieve optimal/comparable results on progress toward sustainable ecological health.

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