

TRANSPORT AND FATE OF PARTICLE-ASSOCIATED CONTAMINANTS IN SMALL URBAN WATERSHEDS

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ABSTRACT

Historical trends and current loadings of particle-associated contaminants in urban environments are rarely quantified. We investigated the transport and fate of particle-associated contaminants in urban streams and lakes through comparison of sediment cores and suspended sediment samples for three lakes in Fort Worth, Texas, U.S.A. Concentrations in suspended sediments compared well to those at the tops of cores for most trace elements but were two to three times larger for many hydrophobic organic contaminants. As a result, for these fluvial systems, sediment cores probably provide a historical record of trace element contamination but could underestimate historical concentrations of organic contaminants. However, down-core profiles suggest that relative concentration histories are preserved in these sediment cores for many organic contaminants (such as chlordane and total DDT) but not all (dieldrin). Elevated concentrations of most organic contaminants in suspended sediments implies that they are preserved in soils, providing a source of legacy contaminants to these fluvial systems for years to come.

RÉSUMÉ

Les tendances et les flux de contaminants associés aux particules sont rarement quantifiés en environnements urbains. Nous avons étudié le transport et le sort des contaminants associées aux particules par comparaison de carottes de sédiments et de prélèvements de sédiments suspendus, dans trois lacs de Fort Worth (Texas, USA). Les concentrations en sédiments suspendus sont proches de celles du haut des carottes pour la plupart des éléments traces, mais sont plus fortes pour beaucoup de contaminants organiques hydrophobes. Il en résulte, en ces systèmes fluviaux, que les carottes probablement produisent un historique des éléments traces, mais qu'elles pourraient sous-estimer l'historique des concentrations de contaminants organiques. Cependant, les profils de beaucoup de contaminants suggèrent que l'historique des concentrations relatives est préservé dans ces carottes pour plusieurs contaminants organiques. Les concentrations élevées de la plupart des contaminants organiques dans les sédiments suspendus impliquent qu'ils sont préservés dans les sols, constituant une source de contamination pour ces systèmes fluviaux pendant les années à venir.

1. INTRODUCTION

Particle-associated contaminants (PACs) pose a threat to biota and humans in aquatic systems because many are persistent, bioaccumulative, and toxic (U.S. Environmental Protection Agency 1997). PACs include trace elements, organochlorine compounds, and polycyclic aromatic hydrocarbons (PAHs). Transport of these compounds and elements is assumed to be dominated by movement on suspended sediments; however, because the chemistry of suspended sediments is rarely measured, this transport is difficult to quantify (Mahler and Van Metre 2003). Instead, numerous researchers have relied on sediment coring for the identification of trends in PACs in fluvial systems (e.g. Charles and Hites 1987; Eisenreich et al. 1989; Van Metre et al. 1997).

The study presented here evaluated the sources, transport, and fate of PACs in Fort Worth, Texas, by measuring PACs in sediment cores from three small urban reservoirs and suspended sediments in the three influent streams (Figure 1). One important objective of the study was to evaluate relations between the chemistry of suspended sediments in transport in urban streams and the chemistry of sediments deposited in lakes downstream. The study was initiated in part because of elevated levels of legacy pollutants in fish in the reservoirs. The term legacy pollutants refers to compounds whose use

has been discontinued, including the chlorinated hydrocarbons chlordane, dieldrin, DDE, and PCBs. Major and trace elements and PAHs also were measured for this study.

2. METHODS

Suspended sediment samples were collected using automated samplers for four storms from the influent streams to each of three small urban reservoirs: Lakes Como, Echo, and Fosdic. Sediment cores were collected from three sites in each of the three reservoirs. Chemical analyses included major and trace elements, organochlorine pesticides, PCBs, and PAHs, and, for the cores, cesium-137 (¹³⁷Cs) activity.

Radiochemical analysis for ¹³⁷Cs activity was performed by gamma spectroscopy. Samples for analysis of major and trace elements were freeze-dried and completely digested using a mixture of hydrochloric-nitric-perchloric-hydrofluoric acids and analyzed for 40 major and trace elements by inductively-coupled plasma/mass spectrometry (ICP/MS) (Briggs and Meier 1999). Mercury was analyzed separately by cold vapor atomic absorption spectrometry (Arbogast 1996). Samples for analysis of organic compounds were extracted, isolated, and analyzed using a variation of the procedures of Foreman et al. (1995) and

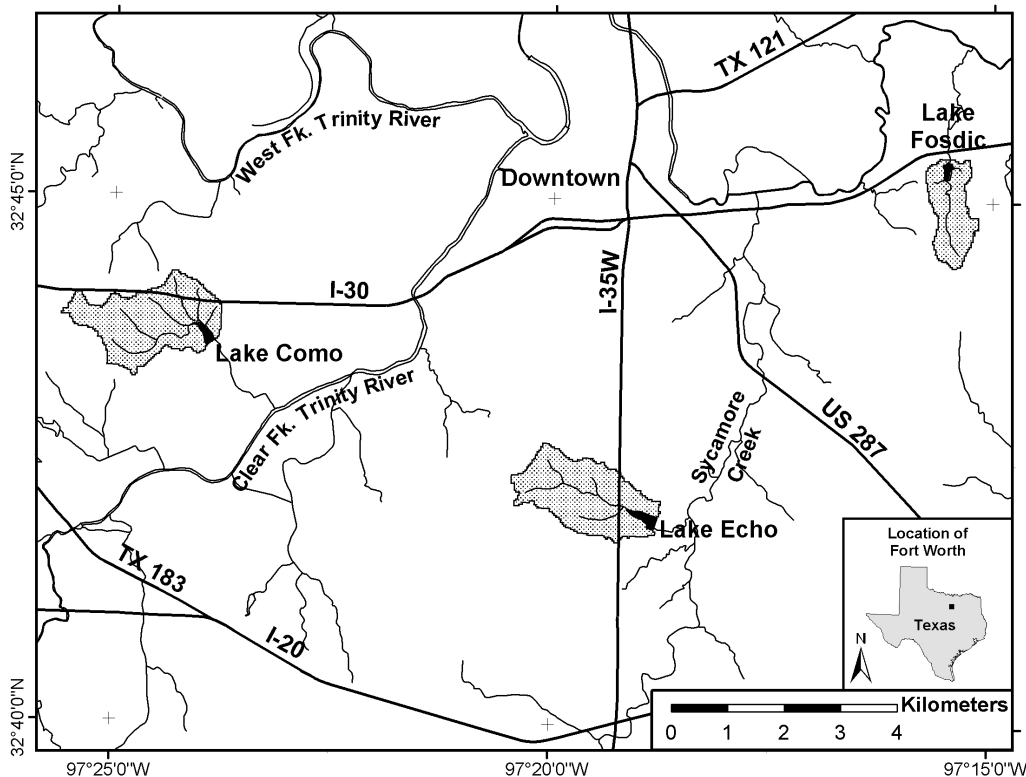


Figure 1. Location of the study lakes (in black) and associated watersheds (shaded areas) in Fort Worth, Texas, U.S.A.

Furlong et al. (1996). Briefly, sediment was extracted with dichloromethane. One aliquot was analyzed for PAHs and alkyl-PAHs by capillary-column gas chromatography (GC) with detection by selected ion monitoring (SIM) mass spectrometry (MS). A second aliquot was analyzed for organochlorine pesticides and PCBs by dual capillary-column gas chromatography with electron capture detection (GC-ECD). DDT, DDD, and DDE reported here are *p,p'*-DDT, *p,p'*-DDD, and *p,p'*-DDE; chlordane is technical chlordane; and total PCB is the sum of the quantified Aroclors 1242, 1254, and 1260.

3. RESULTS AND DISCUSSION

Age-dated sediment cores commonly are used to indicate trends in PACs in the environment (Charles and Hites 1987). In some cases the trends recorded in the sediment core are assumed to be indicative of trends in the influent stream (Van Metre et al. 2001). The data collected in this study provide an opportunity to test this assumption.

Concentrations of selected trace element and organic contaminants were compared between suspended sediments and the tops of sediment cores (Figure 2). Figure 2 shows the ratio of the median concentration at the

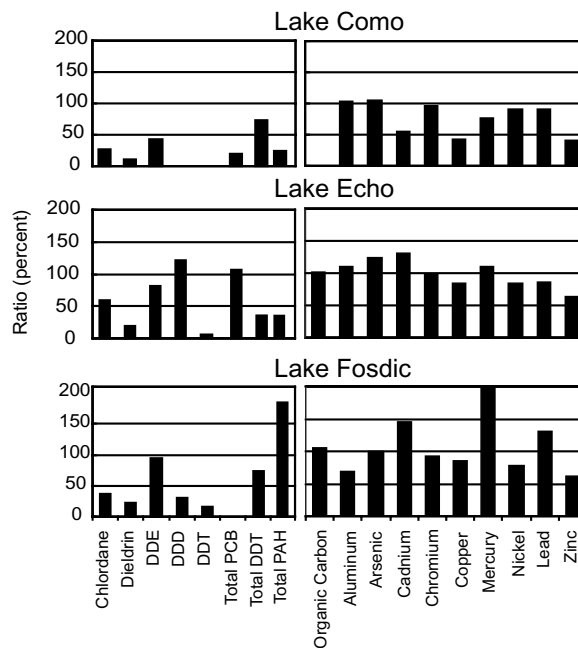


Figure 2. The ratio of median top-of-core concentrations (n=3) to median suspended sediment concentrations (n=4) of selected organic contaminants and trace elements, expressed as a percentage.

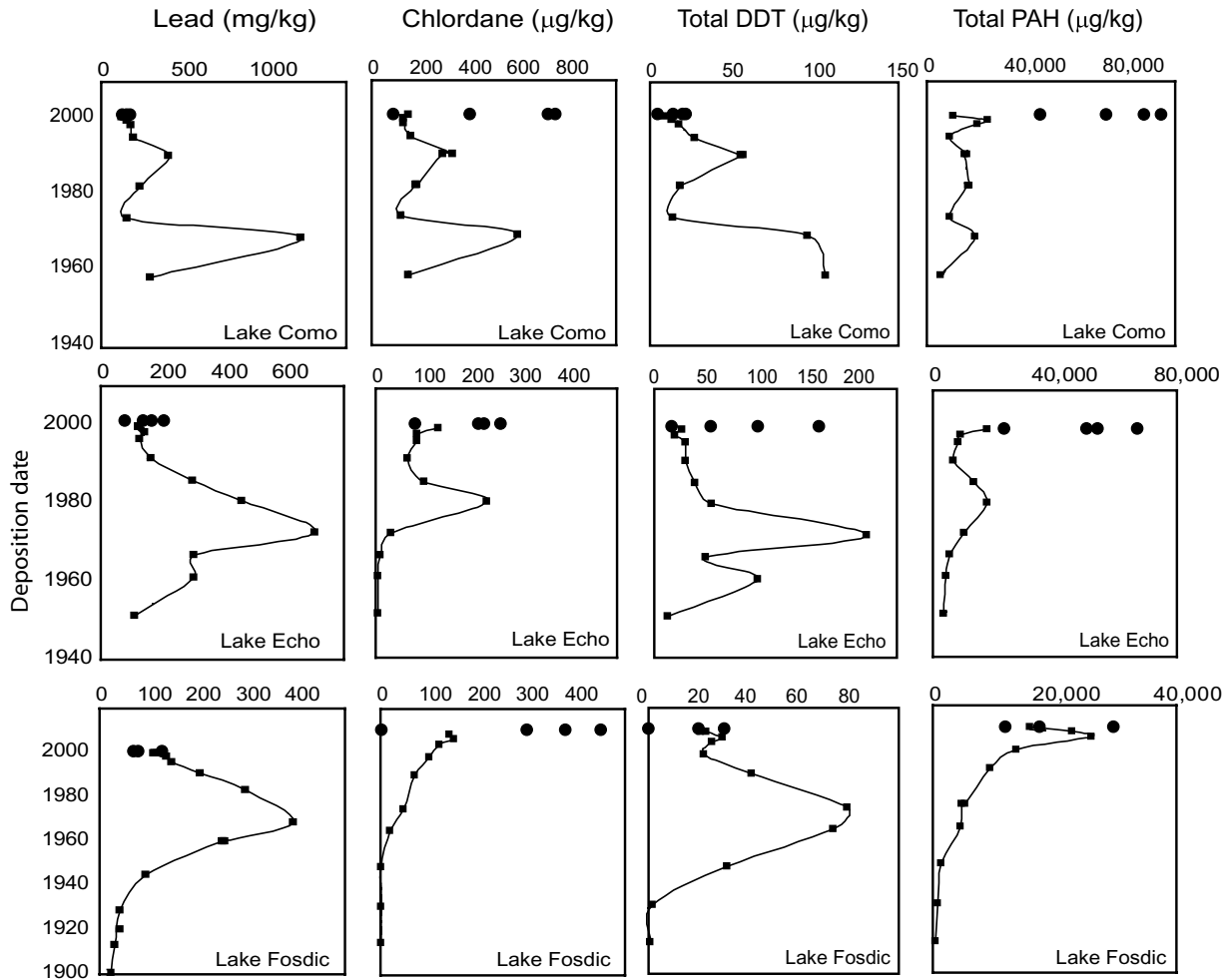


Figure 3. Concentrations and trends in cores and concentrations in suspended sediments of lead, chlordanes, total DDT, and total PAH. Symbols correspond to core samples (squares) and suspended sediment samples from the influent stream (circles).

tops of the three cores from each lake to the median concentration in the four suspended sediment samples from the stream, expressed as a percentage. Concentrations of most trace elements at the tops of cores were roughly similar to those of influent suspended sediments. Concentrations of most trace elements were much less variable in suspended sediments than were those of organic compounds. The similarity between suspended sediments and reservoir sediment concentrations and the low variability between events for trace elements could be partly a consequence of the natural occurrence of trace elements, as proportionally larger background levels translate to relatively less variability in total concentrations.

The similarity between trace element concentrations in sediments from the tops of the cores and suspended sediments suggests that trace element trends preserved in cores reflect historical concentrations in influent streams. Lead, for example, shows pronounced trends in the cores

(Figure 3), mirroring the historical use then removal of lead from gasoline and other reductions in releases of lead brought about by environmental regulations (Callender and Van Metre 1997). The agreement between lead concentrations at the tops of the cores and suspended sediments suggests that these cores not only record trends but could also be reasonable predictors of historical concentrations on suspended sediments in the influent streams. The similarity between suspended and core sediments occurs for many other trace elements (Figure 2). One exception was zinc. Concentrations of zinc at the tops of cores accounted for only 40 to 64 percent of suspended sediment concentrations, the least of any trace element shown. This suggests that zinc could be desorbing from sediment during transport or soon after deposition.

Concentrations of chlorinated hydrocarbons in suspended sediments were highly variable between events at a given site and exceeded concentrations at the tops of cores in

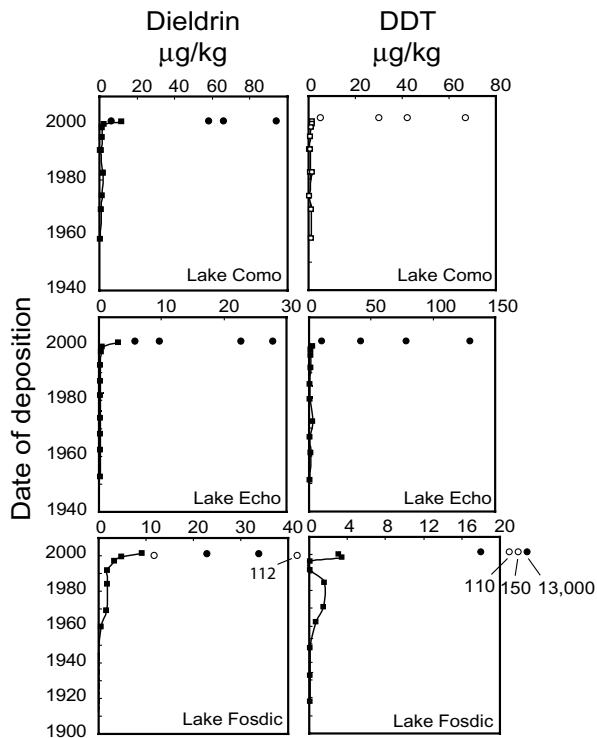


Figure 4. Concentrations and trends in cores and concentrations in suspended sediments of dieldrin and DDT. Symbols correspond to core samples (squares), and suspended sediment samples from the influent stream (circles). Non-detections are shown in open symbols at the reporting level, which varied on the basis of mass of sediment available for analysis.

most cases (Figure 2). Among the chlorinated hydrocarbons, dieldrin and DDT were proportionally the least well represented in the cores, with median concentrations at the tops of cores less than 25 percent those of suspended sediment in all three lake inflows. Concentrations of PAHs in sediments from two of the three lakes were roughly one-third of the concentrations in influent suspended sediments, although in the third lake, Lake Fosdic, PAH concentrations in core sediments were similar to or exceeded those in suspended sediments.

We suggest two hypotheses for differences between organic contaminant concentrations in the suspended sediment and at the tops of the sediment cores. The first is that the average suspended sediment contamination might not necessarily be well represented by the four sampled events. The organic contaminant concentrations associated with the suspended sediment were highly variable (Figure 3), and the sum of precipitation for the events sampled at each site represents less than 7.5 percent of annual precipitation. Furthermore, contaminant loads to the lakes might be greatly influenced by larger events (e.g., 5- to 10- year floods), which were not sampled for this study. A second hypothesis is that once soil is exposed to the water column, there might be loss of some sorbed organic contaminants

through various processes during transport and soon after deposition. These processes include desorption as organic carbon breaks down, bacterially-mediated degradation, and bioaccumulation by benthic biota.

There is evidence, however, that relative concentration histories are preserved for some organic contaminants. For example, the shape of the chlordane profiles down the cores, with pronounced temporal trends that include large peaks in older sediments in two of the three lakes, suggests that chlordane could be stable once deposited and isolated from the water column. Stability of chlordane in sediment cores is consistent with the relatively stable and racemic chiral chlordane signatures seen in cores (Ulrich et al. 2002). The same would appear to be true for total DDT, total PAH (Figure 3), and PCBs (not shown). Many researchers have noted that hydrophobic organic contaminants in sediment can be operationally divided into a "rapidly extractable" fraction and a "sequestered" fraction (e.g., Rockne et al. 2002). Conceptually, it could be that some of this rapidly extractable fraction associated with soils and street dust, the precursors of suspended sediment, is lost to the water column during transport and soon after deposition, and that the sequestered fraction dominates what remains in sediment cores.

DDT and dieldrin have much different trends in cores than the other organochlorine compounds (Figure 4). Concentrations of both increase sharply at the very tops of the cores and are much greater in suspended sediments, when detected, than in the cores. Interpreting these results as increasing environmental occurrence would be inconsistent with historical use. DDT use peaked in the early 1960s, and its use was discontinued in 1972; dieldrin use was voluntarily cancelled in May 1987 (U.S. Environmental Protection Agency 1990). Therefore, an increase in the occurrence of DDT and dieldrin in the environment in the 1990s seems unlikely. Instead, we suggest that the trends seen reflect the continued loss of these contaminants from the sediment after deposition and burial, rather than an increase in occurrence. DDT degrades to DDD and DDE in a transformation that occurs slowly in aerated soils but more rapidly in the presence of water (Guenzi and Beard 1976; Nowell et al., 1999). In those suspended sediment samples in which DDT was detected, DDT accounted for 60 to 77 percent of total DDT (DDT + DDD + DDE) in suspended sediments from the three lake inflow sites with moderate concentrations. The high ratio of DDT to total DDT probably is an indication of recent entry into the hydrologic system rather than recent application (Nowell et al. 1999). In contrast, DDT accounted for only 1 to 26 percent of total DDT in the sediment cores and decreased down core. These data suggest that DDT persists in soils but is converted to DDD or DDE on a time scale of months to years after deposition in the lakes. However, trends in total DDT in cores, composed primarily of the more stable DDD and DDE, seem to be relatively conservative once isolated from the water column (Figure 3). Although no breakdown products of dieldrin were measured, the shape of the core profiles and the concentrations of dieldrin in cores versus suspended sediments strongly suggest that dieldrin,

although persistent in soils (Martijn et al. 1993), is not preserved in these lake sediments.

In summary, comparison of concentrations of contaminants associated with influent suspended sediments to those at the tops of cores suggests that sediment cores probably provide a historical record of trace element contamination, but they may underestimate historical concentrations of organic contaminants in fluvial systems. The elevated concentrations of many of the legacy pollutants in suspended sediments indicate that these contaminants continue to occur in the environment decades after their use was discontinued. In particular, the suspended sediment data demonstrate that contaminants such as DDT, chlordane, and dieldrin continue to be delivered to fluvial systems years or decades after their use has been discontinued.

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