

Ocean Dumping of Containerized DDT Waste Was a Sloppy Process

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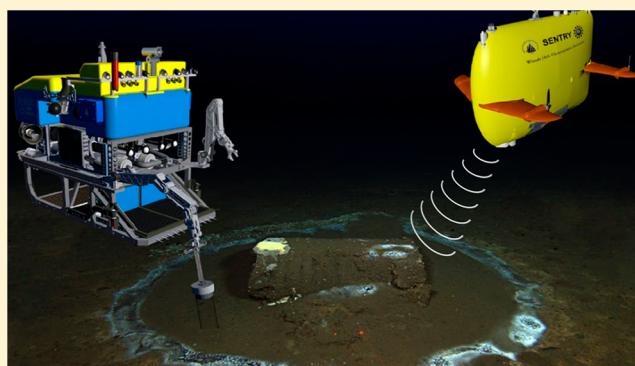
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Supporting Information

ABSTRACT: Industrial-scale dumping of organic waste to the deep ocean was once common practice, leaving a legacy of chemical pollution for which a paucity of information exists. Using a nested approach with autonomous and remotely operated underwater vehicles, a dumpsite offshore California was surveyed and sampled. Discarded waste containers littered the site and structured the suboxic benthic environment. Dichlorodiphenyltrichloroethane (DDT) was reportedly dumped in the area, and sediment analysis revealed substantial variability in concentrations of *p,p*-DDT and its analogs, with a peak concentration of $257 \mu\text{g g}^{-1}$, ~ 40 times greater than the highest level of surface sediment contamination at the nearby DDT Superfund site. The occurrence of a conspicuous hydrocarbon mixture suggests that multiple petroleum distillates, potentially used in DDT manufacture, contributed to the waste stream. Application of a two end-member mixing model with DDTs and polychlorinated biphenyls enabled source differentiation between shelf discharge versus containerized waste. Ocean dumping was found to be the major source of DDT to more than 3000 km^2 of the region's deep seafloor. These results reveal that ocean dumping of containerized DDT waste was inherently sloppy, with the contents readily breaching containment and leading to regional scale contamination of the deep benthos.



INTRODUCTION

Deep ocean disposal of industrial, military, nuclear, and other hazardous waste was a pervasive global practice in the 20th century, the full magnitude of which remains unknown. In the United States, records indicate that 50–97 million tons of industrial waste were dumped at sea,^{1–5} representing an unknown fraction of the total quantity. This ambiguity is due to sparse documentation as well as illegal and clandestine disposal operations. The extent to which containerized waste escaped containment, referred to here as “sloppy dumping”, also remains uncertain. Abandoned industrial waste deep-sea dump sites exist along all coastal states,^{1–5} and one such site, located in the Southern California Bight, is the focus of this study (Figure 1A). According to a technical report by Chartrand et al.,⁶ this area may contain 336000–504000 barrels of acid sludge waste from the production of dichlorodiphenyltrichloroethane (DDT), in addition to various other

containerized waste streams.⁷ Prior to this work, the disposition of this waste and the status of its containment was unknown.

DDT is an organohalide insecticide that was used extensively in the 20th century, leading to a precipitous decline in mosquito-borne malaria morbidity and mortality rates.^{8,9} However, due to its indiscriminate use, recalcitrance, lipophilic bioaccumulation, and adverse impacts on ecosystem and human health, it was banned in 1972 for domestic use in the US.¹⁰ Montrose Chemical Corporation (MCC) was the largest global supplier of DDT, manufacturing ~ 800000 tons of the compound at their Los Angeles County plant from 1947 to

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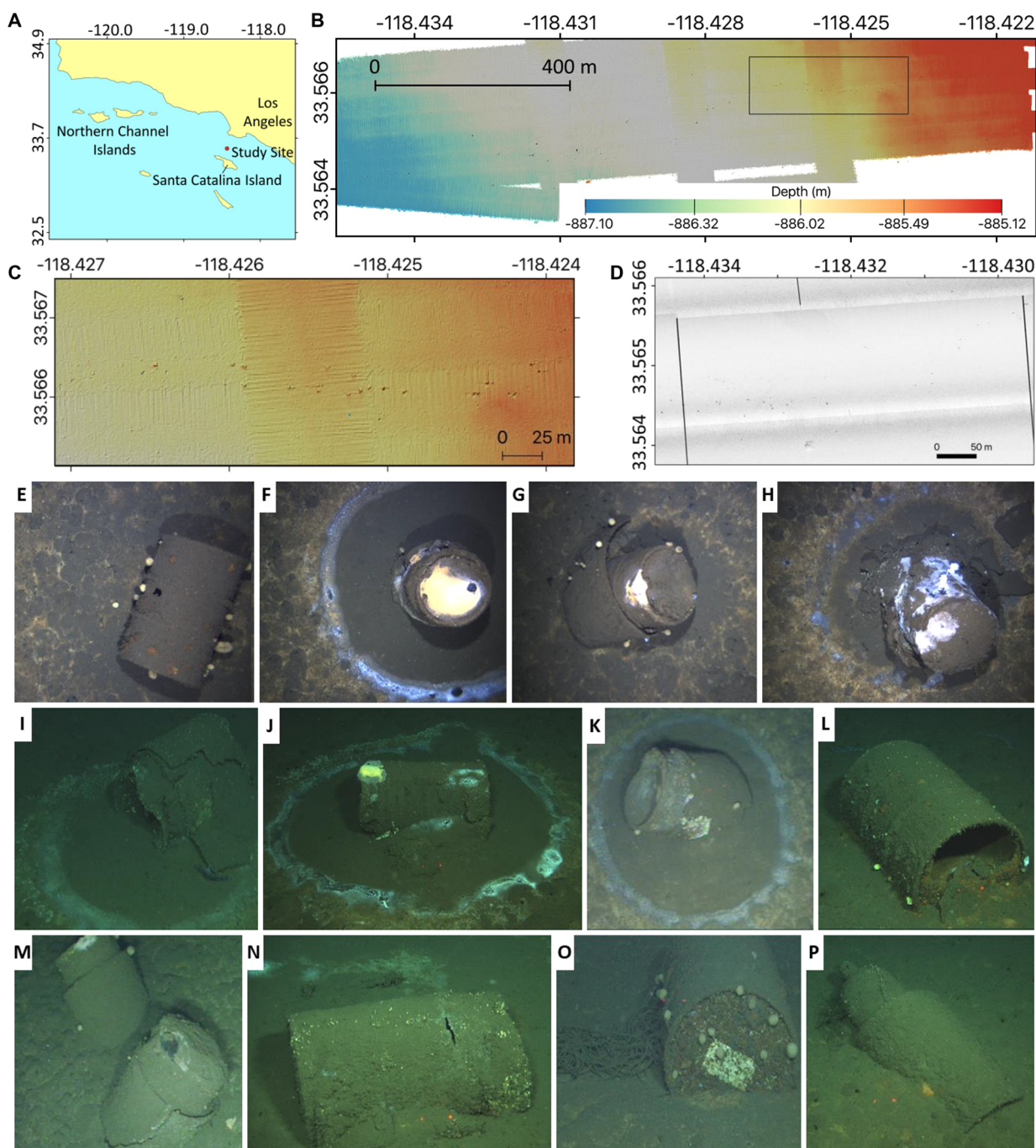


Figure 1. (A) Map of the study region. (B) Multibeam bathymetry from AUV *Sentry* dive 208. (C) Close-up view of selected area from panel B, highlighting topographic anomalies consistent with barrels. (D) Sidescan sonar from AUV *Sentry* dive 208 highlighting anomalies consistent with barrels. (E–H) Images of waste containers from AUV and ROV photo-surveys (I–P).

1982; production following the US ban was exclusively for export.¹¹ The sole product MCC manufactured, technical grade DDT, was sold to other companies for formulation into more dilute commercial insecticide products.¹¹ The composition of technical grade DDT was 65–80% *p,p'*-DDT (the main insecticidal compound), 15–21% *o,p*-DDT, and small amounts of other compounds, including impurities in the form of 1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethylene (DDE) and 1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethane (DDD).^{12–14} Additionally, both DDE and DDD are common breakdown products of DDT, and along with the DDE metabolite, 1-chloro-2,2-bis(4-chlorophenyl)ethylene (DDMU), are fre-

quently detected in the environment. DDE, the result of abiotic or aerobic degradation of DDT, is typically the most abundant compound.^{15–19} We use the shorthand notation DDX to refer collectively to *o,p'*-DDT, *p,p'*-DDT, *o,p'*-DDE, *p,p'*-DDE, *o,p'*-DDD, *p,p'*-DDD, and *p,p'*-DDMU and \sum DDX as the summed concentration of DDT, DDD, DDE, and DDMU (or DDX* for instances where DDMU was not included). In cases where DDT or a metabolite is described without a specified isomer, this refers to the sum of both isomers (e.g., DDE = *p,p'*-DDE + *o,p'*-DDE).

Waste-management practices at MCC included discharge of DDT-laden waste products into storm drains and the sewer

system from 1950 to 1971,^{6,20} leading to contamination of the Palos Verdes Shelf (PVS) with 870–1450 tons of DDT.^{15,20,21} Because of this and other waste, the PVS was added to the US National Priorities List for uncontrolled hazardous contamination, otherwise known as Superfund site designation, and at the time of this publication, remediation is ongoing.

MCC also engaged in another form of DDT waste discharge not accounted for in the creation of the Superfund site: permitted ocean dumping of containerized solid waste. The ocean disposal of these manufacturing byproducts resulted in at-sea dumping of an estimated 2000–3000 barrels per month, equal to ~1 million gallons of waste per year, from 1947 to 1961.⁶ Ocean dumping practices were prescribed by the California Department of Fish and Game, US Coast Guard, and Los Angeles Harbor Department, specifying that waste-hauling companies dump barrels at designated locations in the basins off the coast of Southern California, ~16 km offshore; however, short-dumping at locations closer to shore was common practice.^{6,22,23} Dumping of other containerized waste, including caustic and acid waste produced by petroleum refineries, also occurred in these areas.^{6,7,24}

The DDT contents of MCC's waste barrels was substantially lower than the composition of the product they sold. While not explicitly documented, it has been estimated to contain 0.5–1% DDT, totaling 384–767 tons of DDT; the remainder was a mixture of sulfuric acid, organic substances, and water.⁶ However, a patent on DDT acid waste treatment describes this mixture as about 2% DDT, 72% sulfuric acid, 25% *p*-chlorobenzene-sulfonic acid, with traces of water and hydrochloric acid.²⁵ Thus, we surmise that the total DDT content of waste in ocean-dumped barrels may have been as high as 2%, resulting in the revised range of 0.5–2%, and a total discharge of 384–1535 tons. The upper limit of this revised estimate is comparable to DDT released at the White Point outfalls, on the nearby PVS Superfund site (870–1450 tons of DDT).^{15,21}

In addition to the ambiguity about the total amount of DDT dumped into the deep ocean as containerized waste, several other factors contribute to the complexity of understanding the fate and impact of these materials. First, minimal record keeping was performed as to what, where, when, and how waste was dumped. Second, site access is limited and costly due to the ~900 m site depth, which requires substantial resources (e.g., the use of specialized submersibles for identifying relatively small seafloor anomalies and for benthic sampling, as well as the cost of the associated vessel). Third, potential shelf sources^{16,26,27} complicate interpretation of DDT origin. Fourth, decades of overprinting from environmental processes such as burial, suspension, redistribution, and biodegradation have undoubtedly altered the site's chemical inventory.^{15,17,28,29} Fifth, the hydrophobic nature of DDT³⁰ and its potential association with organic matter, including sorption to hydrocarbons, has previously been found to influence localized concentrations³¹ and may affect DDX distributions in basin sediment. Sixth, spatial variability related to the location of dumping provides for an expectation of heterogeneity. Finally, the integrity of waste containers is unknown, precluding an accurate assessment for the spatial distribution of contamination. Given these ambiguities, the scale of ecological effects is uncertain and the long-term fate of the disposed material remains unknown.

In this work, we describe a nested approach to the exploration of deep ocean waste dumpsites as applied to the suboxic San Pedro Basin (SPB), located off the coast of

southern California (Figure 1A). We first apply autonomous underwater vehicle (AUV) technology to identify sea floor anomalies consistent with containers and to collect associated images of the sea floor. We then use a remotely operated vehicle (ROV) to collect sediment cores for analysis of chlorinated hydrocarbon and hydrocarbon distributions, to generate insights into the industrial processes that gave rise to the contamination, as well as the weathering and biogeochemical processes that occurred since deposition. Finally, we apply these findings to provide a framework for differentiating the major sources of DDT contamination at the regional scale. This nested approach has considerable potential for other areas of seafloor exploration, in addition to exploration of deep-sea waste disposal sites.

MATERIALS AND METHODS

Mapping and Sampling. These sites were accessed using the AUV *Sentry* and the ROV *Jason*. The AUV *Sentry* was deployed to collect high-resolution multibeam echosounder (MBES) bathymetry,³² which was processed shipboard to identify positive elevation anomalies consistent with barrels. The ROV *Jason* was deployed to enable closer inspection of the observed features and sampling of the sediments. Following ROV retrieval, sediment cores were sectioned at 2 cm intervals and samples stored at –20 °C for chemical analysis. Further description of the mapping and sampling information is provided in the *SI Methods*.

Analytical Methods. Extensive chemical analysis by means of one-dimensional and comprehensive two-dimensional gas chromatography (GC and GC × GC) with mass spectrometry (MS), flame ionization detection (FID) and high resolution time of flight mass spectrometry (HR-ToF-MS) were conducted to analyze chlorinated and other hydrocarbons as described previously,^{33–37} and the methods used in this study are described in full in the *SI Methods*.

DDX Mass Balance. DDX source attribution for each core-top sample³⁸ was calculated assuming a mass balance of two end-members: sediment near to the White Point sewage outfalls ($\sum \text{DDX} : \sum \text{PCB} = 13.8$) and dumped barrels that contain DDX but no PCBs ($\sum \text{DDX} : \sum \text{PCB} = \infty$). The following mass balance results:

$$f_d = 1 - R_{\text{PVS}}/R_s \quad (1)$$

where f_d is the fraction of $\sum \text{DDX}$ attributed to deep-sea disposal for a given sample; R_{PVS} is the $\sum \text{DDX} : \sum \text{PCB}$ ratio assumed for the PVS endmember (13.8); and R_s is the $\sum \text{DDX} : \sum \text{PCB}$ ratio for a given sample. The full list of compounds, concentrations, method detection limits and other relevant information about data processing for figure plots is included in the *SI Methods*.

RESULTS AND DISCUSSION

Discovery and Observations. According to a 1985 technical report by Chartrand et al.,⁶ practices for industrial waste dumping at specific locations in the SPB and Santa Monica Basin (SMB) were established in 1947 by the California Department of Fish and Game, US Coast Guard, and Los Angeles Harbor Department. However, dumping at unassigned locations was known to be common practice.²³ One of the assigned dumpsites (Figure 1A) is located near an existing methane hydrate study site, and we were twice afforded the opportunity to use robotic marine technology to

explore the seafloor in this area. Samples for the current study were collected from two adjacent locations (J2-603 and J2-746) within the study site (Figure 1A and Figure S37).

In 2011 and 2013, we developed and applied a nested approach to investigate seafloor features near the assigned dumpsite in the SPB. This approach included use of AUV *Sentry* for identification of seafloor anomalies by multibeam echosounder (Figure 1B,C), side scan sonar (Figure 1D), and stereopaired imaging (Figure 1E–H), followed by the use of ROV *Jason* for detailed visual surveys (Figure 1I–P) and sample collection. We focused on the landward side of the assigned dump area, with logic dictating that shorter trips would be desirable for those who conducted dumping operations. About 60 waste barrels were visually located at a water depth of ~900 m. All barrels were partially buried in the sediment, though it was not possible to differentiate initial emplacement versus subsequent sedimentation. Some of the barrels were clearly not intact (Figures 1L and S4,S6), including barrels with apparent puncture marks (Figures 1E,N and S22), while the presence of gas inside other barrels, observed during sampling, suggests that they were at least partially intact. Different barrel and cylinder types were present at the site (Figures 1E–P and S1–S35), implying multiple waste origins, consistent with the report of Chartrand et al.⁶ The stereopair imaging from AUV *Sentry* was used to estimate the volume for several of the barrels and cylinders (Figure S36). Some barrels had dimensions consistent with standard 110-gallon and smaller drums, while others were consistent with XL-type gas cylinders. There is evidence to suggest that the waste was dumped purposefully. Many barrels occurred in groups of identical appearance (Figures 1M and S18–S21). Concrete footings for barrels and cylinders chained at the neck to a footing around their base suggest intentional ballasting. Additionally, the distribution of barrels on the seafloor corresponds to an imprecise line, as would occur if barrels were offloaded from a moving barge (Figures 1C and S37–S42).

The biota associated with barrels at this low-oxygen (<10 μM) site^{39,40} is fundamentally different from other settings where barrels serve as artificial substrate for the growth of sessile organisms, including sponges, anemones, and tunicates, and provide habitat for crabs, starfish, and brittle stars.^{41–43} In those settings, sessile organisms sometimes form distinct structures on barrels, resembling bioherms.^{41–43} In this study, sponges were observed on some barrels, for example, Figure 1E,G,O, and one of the barrels apparently hosted dozens of snails (Figure S4C). However, rather than promoting substantial macrofaunal growth, the barrels in this oxygen-limited environment primarily host microbial communities, including apparent mats of filamentous sulfur bacteria atop some barrels and ring-structured microbial mats on the sediment surface surrounding some barrels (Figures 1F,H–K and S2–S35). In some instances, the bordering microbial ring formation differentiates the appearance of the sediment surface inside versus outside the ring (Figures 1F,J,K and S7, S25, S27–S29, and S35).

Disposition of Chlorinated Hydrocarbons in Sediments. Sampling was conducted under the presumption that many of the barrels contained DDT, based on the report of prolific dumping at or near the study site.⁶ Using the ROV *Jason*, 19 sediment cores were collected (four in 2011 and 15 in 2013) (Tables S1–S6) to reconstruct the chronology, magnitude, and spatial distribution of contamination, including

an association with barrels and their microbial ring features. Target analytes included isomers of DDT and its degradation products, DDD, DDE, and DDMU. While these compounds have been monitored extensively at the PVS, few analyses have been conducted in the SPB, despite reported waste disposal operations in the region.^{38,44–46} DDT and its degradation products were present in all cores, and the concentrations were highly variable (Tables S1–S6). Notably, proximity to barrels does not appear to control $\sum\text{DDX}$ (Figures S37 and S43–S45 and Table S7); sediment with the highest $\sum\text{DDX}$ was collected away from barrels, including one core with high $\sum\text{DDX}$ concentrations (core 11-1A) taken at a conspicuous mound. These findings indicate the disposal process was inherently sloppy, which we define here as intentional disposal of containerized waste wherein the waste ultimately escapes the container.

The DDX chemical data set consists of 386 concentrations, comprised of four metabolites across five depth horizons (at 2 cm resolution to a depth of 10 cm) for 19 cores (two of which were subsampled, see Methods) and is summarized in Table S8. Here, we consider the findings in terms of three discrete sediment intervals (Table S1–S3) representing different eras based on the assumption of uniform sedimentation at a rate of $\sim 1 \text{ mm y}^{-1}$:⁴⁷ postdisposal (core-top 0–2 cm; after domestic DDT use and disposal ended), peak disposal corresponding to dumping operations (midcore 4–6 cm), and predisposal (down-core 8–10 cm; preceding widespread DDT use or disposal). Depth profiles of $\sum\text{DDX}$ for representative cores from the sampling sites (J2-603 and J2-746) are shown in Figure 2 along with the metabolite distribution by depth horizon.

The postdisposal (core top) $\sum\text{DDX}$ concentrations are variable (Table S1), with a maximum of $\sim 800 \text{ ng g}^{-1}$ and a mean of 106 and 201 ng g^{-1} at the J2-603 and J2-746 sites, respectively (Figure S46A). Postdisposal sediment overlying high DDT intervals is not systematically enriched in $\sum\text{DDX}$ compared to other samples. DDE was dominant in many samples. The prevalence of DDE may be due to the combination of DDE originating from waste in barrels, and an additional input of DDE from the PVS, where DDE is an abundant contaminant.¹⁵ Data from another study reveals a similar trend of relatively low $\sum\text{DDX}$ surface concentrations (dominated by DDE) overlying very high $\sum\text{DDX}$ intervals in the SPB.²⁴ These observations are consistent with ongoing burial of DDX and only minor amounts of vertical redistribution post deposition.

However, substantial DDT concentrations were also observed in surface sediment not associated with underlying intervals of high DDT, indicating that a recent or ongoing source is also present. This is consistent with two samples collected for a study by the Southern California Coastal Water Research Project (SCCWRP), which also found elevated surface concentrations of $\sum\text{DDX}$.³⁸ Importantly, one of our samples and one of the SCCWRP samples from the SPB have elevated concentrations of DDT, in excess of that measured for the highest $\sum\text{DDX}$ sample at the PVS,³⁸ suggesting a contemporary, nonshelf source of DDT to the SPB. These observations are consistent with the possibility that the contents of the barrels are slowly leaking or that DDT remobilization from buried sediment is occurring with spatial heterogeneity, as might be caused by limited burrowing activity of infauna.

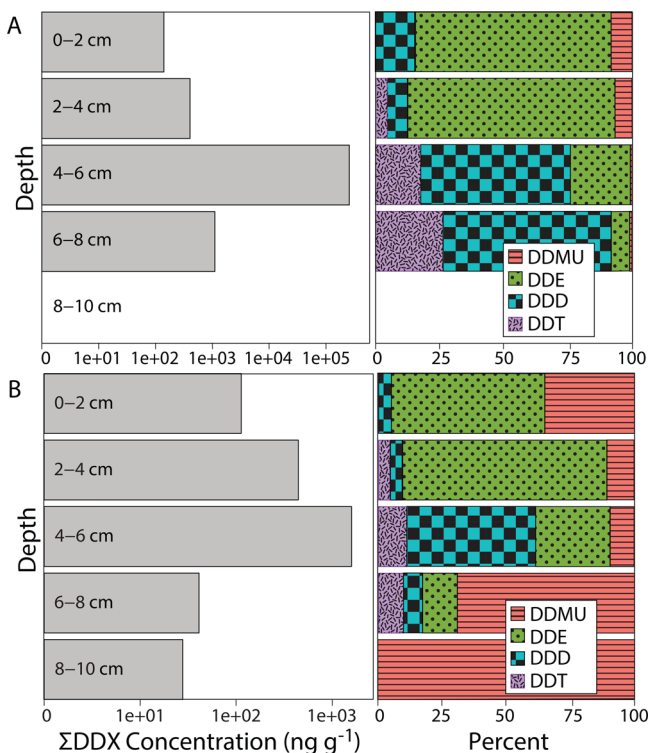


Figure 2. Σ DDX depth distribution for two representative cores, one from each expedition: (A) J2-603 in 2011 and (B) J2-746 in 2013. Concentrations are shown on a log scale (note different axes). Shown at right is the distribution of DDX compounds corresponding to each depth interval shown at left.

The 4–6 cm depth interval corresponds to the recorded period of disposal. Measured Σ DDX concentrations from the J2-603 samples are low in two of four cores, while the other two cores have elevated concentrations, one with Σ DDX of $257 \mu\text{g g}^{-1}$, the highest of our data set (Table S5). For the samples collected at J2-746, both the highest Σ DDX concentration (1520 ng g^{-1}) and the mean (370 ng g^{-1}) were substantially lower than the concentrations meas-

ured at J2-603 ($257\,000 \text{ ng g}^{-1}$ and $64\,600 \text{ ng g}^{-1}$, respectively; Table S8). Again, this is suggestive of a nonuniform distribution of discarded waste, demonstrating the occurrence of hotspot contamination including elevated proportions of DDT.

For the two cores with the highest Σ DDX in the 4–6 cm interval (cores 11-1A and 11-1B; Table S5,S6), the sediment from this interval was split (see the Methods), and the concentrations for each split were found to differ by an order of magnitude. The Σ DDX* for core 11-1B and its split (S-core 11-1B) were $256 \mu\text{g g}^{-1}$ and $26 \mu\text{g g}^{-1}$, respectively while core 11-1A and its split (S-core 11-1A) had concentrations of $96 \mu\text{g g}^{-1}$ and $7.9 \mu\text{g g}^{-1}$. These data highlight substantial heterogeneity in chemical concentrations across different spatial scales: between the two adjacent sites, within a single site (e.g., between different cores collected during a single dive), as well as within a 2-cm core section. Large differences in DDX concentration have recently been noted on the centimeter scale for PVS sediment pore water,³¹ and the patchy concentrations of DDX may be influenced by the hydrophobicity of DDT³⁰ and its sorption to hydrocarbons or organic matter present in sediment.³¹

In the predisposal sediment horizon (8–10 cm), most of the Σ DDX concentrations, as well as the mean and median Σ DDX, are substantially lower compared to those of the overlying intervals (Table S3). Nonetheless, measurable concentrations are apparent in our samples as well as in a core previously collected near this site for another study (NOAA core V),²⁴ consistent with slight downward redistribution in the sediment. Notably, DDMU in the 8–10 cm depth horizon from the J2-746 cores is common and accompanied by little or no other DDX compounds, indicating this is not an artifact of coring (Figure S46C). The presence of DDMU to the exclusion of other metabolites in this depth horizon suggests downward transport and subsequent degradation are occurring in situ. For example, DDE can anaerobically degrade to DDMU.¹⁸

Distinguishing Contamination from Shelf and Deep Basin sources. The PVS Superfund site is among the most

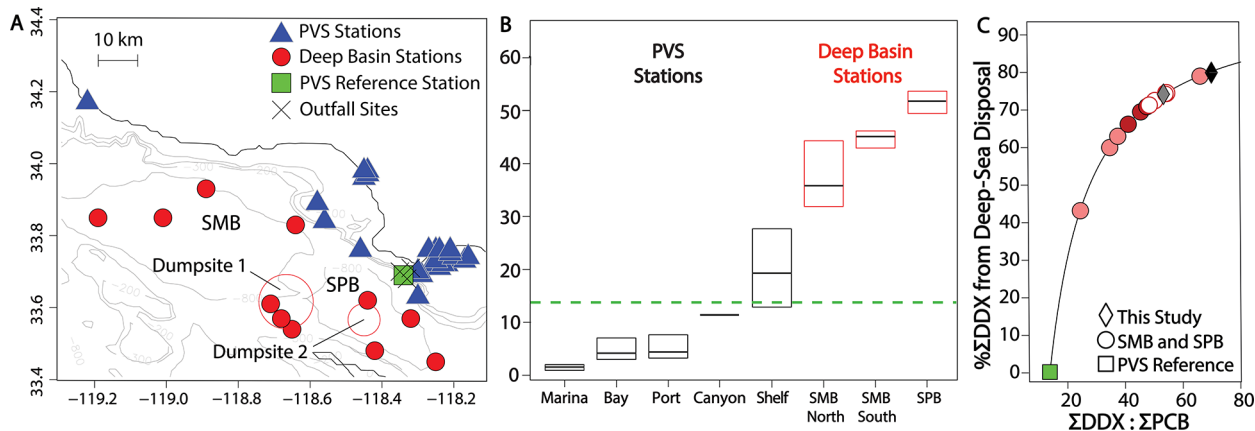


Figure 3. (A) Bathymetric map showing SCCWRP core-top sampling locations used for comparison in this study. Note that leftmost station is NW of the PVS. Also shown are Dumpsites 1 and 2 (in the SMB and SPB, respectively). (B) Ratio of the Σ DDX: Σ PCB by station type with median (line) and the interquartile range (box) shown; the green dashed line shows the end-member ratio for the PVS reference site. (C) Percent of Σ DDX attributed to deep-sea disposal by location, as determined by the mixing curve, derived from eq 1 (see DDX Mass Balance). The detailed (color) legend is as follows: red outline, white fill: SPB; light red fill: SMB north; dark red fill: SMB south; black diamond: Core 11-1B; grey diamond: minimum estimate determined using method detection limits for Σ PCB for Core 11-1A; green box: PVS reference site. For data from this study, Σ DDX* and Σ PCB* were used.

contaminated sites globally for chlorinated hydrocarbons, with a surface sediment \sum DDX concentration of up to $6.5 \mu\text{g g}^{-1}$ measured recently near the White Point outfalls.³⁸ The PVS is commonly considered the primary source of DDT contamination to the Southern California Bight, for which 71% of surface sediments are enriched in \sum DDX.⁴⁵

We asked what contribution deep ocean dumping could have on the DDX inventory of the two offshore basins in this region, an area comprising over 3000 km^2 . To make this estimate, we developed a mass balance using the proportion of \sum DDX to polychlorinated biphenyls (\sum PCB), an approach similar to that suggested by Venkatesan.²⁴ PCBs are similar to DDTs in terms of hydrophobicity, recalcitrance, and years of disposal, but were neither manufactured in California nor present in MCC waste barrels.^{30,39,47–49} Importantly, PCBs were commingled with DDT in the Los Angeles County Sanitation District outfalls at White Point.⁴⁶ We chose the most heavily \sum DDX-contaminated core sample at the White Point outfalls (\sum DDX: \sum PCB = 13.8) (Figure 3A,B) as an endmember representative of the Palos Verdes Shelf.³⁸

An analysis of core-top \sum DDX: \sum PCB from a recent monitoring campaign by SCCWRP³⁸ reveals that the deep SPB ($n = 4$) and adjacent Santa Monica Basin (SMB) ($n = 7$) (Figure 3A) contain ratios of 48.2–54.1 and 24.3–65.8, respectively, substantially greater than for the PVS and other shallower environments (Figure 3B and Table S10). Application of mass balance to these deep basin samples and cores from this study (using \sum DDX*) yields a \sum DDX fractional contribution for deep sea disposal ranging from 71 to 80% for the SPB and 43–79% for SMB (Figure 3C), with some percentages as minimum estimates (the method detection limit values were used when \sum PCB was below detection limits).

To further validate the assumptions inherent to this approach, diagnostic characteristics of DDX originating from deep disposal were identified and assessed. Here, we examine high-concentration DDX cores from this study as well as from a core collected in the SPB in 1989, reported in a NOAA technical document²⁴ (Table S9). First, the ratios of \sum DDX*: \sum PCB are consistent with the premise that deep ocean waste disposal is the source of persistent DDX contamination in the SPB. Second, ocean-dumped barrels contained waste from technical-grade DDT, which has approximately a 4:1 ratio of *p,p'*-DDT to *o,p'*-DDT.^{14,50} The cores from this study yield ratios of 4.05 and 4.50; NOAA core data are also in agreement. Third, high \sum DDX* was also measured in these samples and is dominated by DDT or DDD (>50%), inconsistent with material transported from the PVS which is dominated by DDE and DDMU.^{15,26,38} Finally, sediment strata containing high \sum DDX correspond to the timing for containerized waste dumping.⁶

Although the spatial resolution of sampling is overly coarse, these results are consistent with a scenario in which a majority of DDX in the two borderland basins adjacent Los Angeles derive primarily from deep ocean disposal, rather than the highly publicized disposal to the PVS.

Chemical Complexity of Discarded Waste. To better understand the provenance of waste dumped at the site, we conducted additional chemical analysis including GC-FID on J2-603 sediment (Figures S47–S49) and additional analyses on the sediments with the highest concentrations of DDT (2–4 and 4–6 cm depth horizons of core 11-1A and 4–6 cm of core 11-1B). The occurrence of multiple distinct petroleum

fractions was identified by GC-FID and GC-MS in the form of a multimodal distribution of the unresolved complex mixture (Figure 4B), triggering subsequent analysis by GC \times GC-FID, GC \times GC-ToF-MS and GC \times GC-HR-ToF-MS (Figure 4 and SI part 2 and part 3).

Using comprehensive two-dimensional chromatography, these modes were resolved into five mass islands in chromatographic space (Figure 4), four of which we attribute to industrial petroleum distillates, based on the pattern of mass distribution. The first eluting mixture comprises a minor fraction of the total mass, and contains branched and cyclic hydrocarbons containing ~ 9 –15 carbons. The compounds in this mass island are primarily branched, isoprenoidal, and straight-chain alkanes along with C_0 – C_4 decahydronaphthalenes (decalins) with the C_2 -decalins as the most abundant members of this suite of compounds. The second eluting mixture contains aromatic and cyclic hydrocarbons with ~ 12 –20 carbons, likely representing a light distillate cut similar to diesel fuel. Compounds of note in this mixture include a distinctive family of *m*-xylenes substituted with tertiary butyl or other tertiary alkyls (Figure 4D). The abundance of these unusual compounds suggests formulation by a second industrial process, beyond simple distillation. This moderately polar mixture has a lower boiling point than for DDT, making it a candidate solvent for extraction and purification following DDT synthesis. The third mass island contains compounds commonly found in petroleum: tricyclic terpanoids (cheilanthanes), a tetracyclic terpanoid, and two steranes with prominent *m/z* 218 ions (diginane and 20-methyldiginane). The fourth mixture is a petroleum residue that is dissimilar in its biomarker distribution to regional oil seeps of the Monterey Formation⁵¹ (Figure 4E). This fourth mixture appears to be consistent with a “tank bottom” residue left behind after distillation, based on the presence of 2-methylantracene and a tentatively identified (by GC \times GC retention position) hopene structural analog to $17\alpha(\text{H})$ -22,29,30-trinorhopane—both indicators of petroleum refining.⁵² Collectively, the presence of four apparent petroleum distillate cuts suggests complex petrochemical use during DDT manufacture, potentially overprinted by mixing of waste streams.^{6,7,23}

The mass resolving power of GC \times GC-HR-ToF-MS enabled a search for organo-chlorine ions across the full GC \times GC chromatogram (Figure 4A, SI Part 2), capitalizing on the mass difference between chlorine isotopes. A complex mixture of mainly chlorophenyl-containing compounds was identified (Figure 4A) using the identification criteria indicated, described in full in SI part 2 and part 3. In addition to DDT and common degradation products (DDE, DDD, and DDMU), several notable compounds were detected, including dicofol isomers (peak 15), tris(4-chlorophenyl)methane isomers (TCPMe, peaks 16 and 17), dichlorodiphenylmethane isomers (DDM, peaks 3 and 4), and dichlorobenzophenone isomers (DBP, peaks 5 and 6) in addition to a variety of related compounds for which mass spectra did not match known compounds (SI part 2 and part 3). Dicofol, synthesized from DDT, is an acaricide that is currently in use in the United States and was recently classified as a candidate persistent organic pollutant in the Stockholm Convention.^{53–55} Atmospheric and current-driven transport has been previously noted for dicofol, and this compound was detected in low concentrations ($<15 \text{ ng g}^{-1}$) in sediment at 10 SCCWRP stations, primarily in Los Angeles/Long Beach bays and ports.^{38,54–55,56} Since dicofol is currently in use, it is difficult to

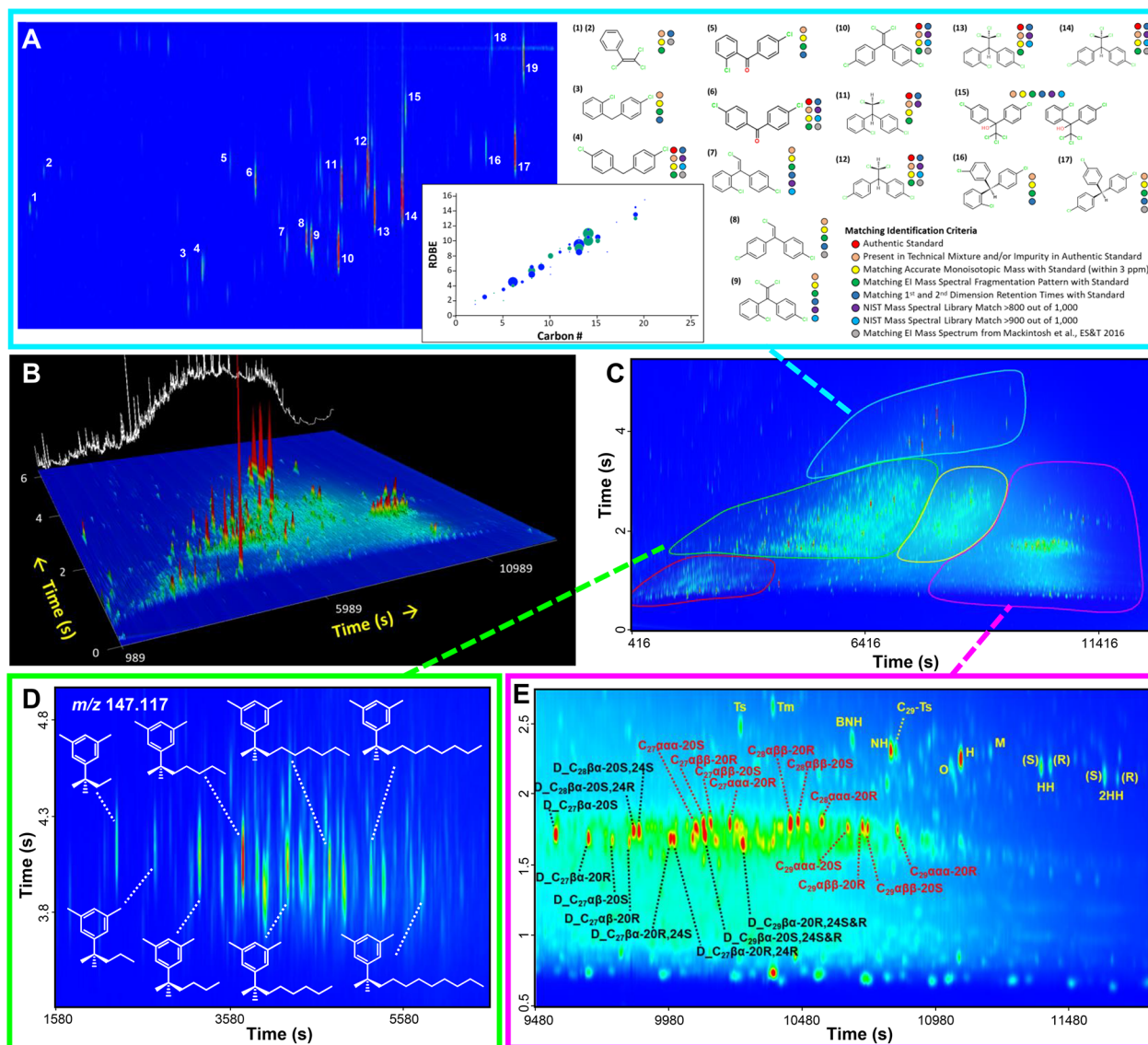


Figure 4. Chemical composition of DDT waste from core 11-1A, color coded by chromatographic island. (A) Chlorine-containing compounds identified by unique mass assignment with GC × GC–HR–ToF–MS. Peaks labeled 1–17 are each chlorinated, with a subset of structures identified as described in the matching identification criteria. Compound identities are as follows: (1)(2) Trichloroethenyl benzene (3) Bis(chlorophenyl)-methane isomer A (4) Bis(chlorophenyl)-methane Isomer B (5) 2,4'-Dichlorobenzophenone (6) 4,4'-Dichlorobenzophenone (7) *o,p'*-DDMU (8) *p,p'*-DDMU (9) *o,p'*-DDE (10) *p,p'*-DDE (11) *o,p'*-DDD (12) *p,p'*-DDD (13) *o,p'*-DDT (14) *p,p'*-DDT (15) Dicofol Isomers (16) 2,3',4"-TCPMe (17) 4,4',4"-TCPMe. Inset shows the relationship between ring double bond equivalents (RDBE) and carbon number, highlighting prevalence of chlorinated aromatics. (B) GC × GC–ToF–MS chromatogram shown in mountain view, with the total signal collapsed in white at rear to simulate a one-dimensional chromatogram. (C) GC × GC–ToF–MS chromatogram shown in plan view, color coded to highlight five mass islands. (D) Partial GC × GC–ToF–MS chromatogram illustrating a putative family of *m*-xylenes substituted with tertiary alkyl groups. (E) Partial GC × GC–ToF–MS chromatogram annotated to identify common petroleum biomarkers.

determine its long-term fate in the environment, due to a lack of temporal resolution for monitoring data (e.g., nonsurface sediment). The presence of dicofol in buried strata observed here hints at its persistence in the environment. TCPMe has been described as an inadvertent byproduct of DDT manufacturing¹² and has been detected globally in birds and mammals,^{57,58} including in Southern California dolphins and pinnipeds.^{59,60} Concentrations of DDX compounds in these dolphins were greater than 1 order of magnitude higher than in dolphins from other locations around the world, and TCPMe (an unmonitored compound) was second only to DDE.⁵⁹ Under environmental conditions, TCPMe may be much more persistent than DDT and its analogs; however, despite

evidence of its persistence and bioaccumulation, TCPMe is rarely studied in marine sediments.⁶¹ DDM and DBP are anaerobic degradation products from dehalorespiration of DDT,¹⁷ and recent work suggests that DBP may be a main end product of DDT degradation.⁶² The presence of DDM and DBP at low relative abundance suggests the trace occurrence of this anaerobic microbial process is associated with these wastes.

Biogeochemical Processes. Several lines of evidence indicate that dumped wastes structure benthic biogeochemical processes, including the occurrence of microbial mats on the barrels, the microbial ring structures that surround some barrels, and the presence of putative metabolic products from

dehalorespiration. Based on their filamentous appearance, the mats likely comprise dominant populations of sulfide-oxidizing bacteria. Sulfide sources from underlying sediment may include sulfate-reducing bacteria, coupled to the organic components spilled from the waste containers, or driven directly by reduced metal surfaces of the barrels.⁶³

Core collection also revealed that sediment near some barrels was supersaturated with gas, which began bubbling rapidly upon core removal, despite the ambient pressure of 91 bar. Gas ebullition provides one possible explanation for the distinct appearance of the sediment surface immediately surrounding some barrels as seen in Figure 1F,K,L, though the process of gas generation remains unknown. Initially, we suspected active methanogenesis, facilitated by the deposited waste, caused gas buildup. However, measurements of interstitial methane concentrations from cores (Table S11) within 1 m of gas release yield a maximum concentration ~ 19 μ moles per liter of bulk sediment, which is orders of magnitude too low to support a free gas phase. Nonetheless, in one core, the methane concentration increased with depth more than is typical⁶⁴ and thus, the source of the observed gas remains uncertain; we therefore consider other possible sourcing mechanisms. One potential source of the gas is from the barrels themselves, some of which were also observed during sampling to contain a gas charge. While possible, it is difficult to envision how the gas would migrate downward into the sediment and laterally away from the barrel. A second potential source is nonmethane microbial gases produced through respiration (CO_2), denitrification/anammox (N_2 , N_2O), or fermentation (CO_2 , H_2). Still, it remains difficult to envision how these gases would accumulate to the point of ebullition at 91 bar ambient pressure. A third potential source is cathodic H_2 derived from electrochemical reactions^{65,66} involving corrosion of metallic components of the barrels. A fourth potential source is from acidification of bicarbonate and carbonate to CO_2 , driven by highly acid material in the barrel. For any of these mechanisms, it remains unclear how the gas phase is sustained near to the sediment surface for extended periods of time, given dissolution and diffusion.

Environmental Impacts. Pervasive disposal of wastes to the coastal ocean in the mid-20th century was ill-conceived insofar as the potential for oceanic impacts was all but ignored. From the chemical plants of Southern California, barrels of chlorinated (and other) wastes were dumped into a low energy, low-oxygen benthic environment that is typically incapable of supporting respiratory demands for large macrofauna. Contrasting with the potential of this site for long-term sediment burial, the disposal process was inherently sloppy, with the discarded waste escaping containment and entering the sedimentary system. The resulting legacy includes a striking persistence of the discarded xenobiotic wastes, including DDT and other chlorinated organics, as well as petroleum-derived residues.

Despite typically low oxygen concentrations, the San Pedro and Santa Monica basins host some infauna and experience occasional flushing events that allow for additional benthic macrofauna.^{39,40} To understand the potential toxicity of sediments, we compared our results with the NOAA sediment quality guidelines for the effects range median (ERM), above which adverse effects are likely.⁶⁷ For $\sum\text{DDX}^*$, the ERM is 46.1 ng g^{-1} ⁶⁷ (note that in this study the *o,p'*- isomers are included for assessing $\sum\text{DDX}^*$ values). Across samples from the top 6 cm of sediment cores in this study, 86% exceed the

ERM value for $\sum\text{DDX}^*$, and the median concentration is 4.8-fold greater than the ERM. Hotspot contamination exceeds the ERM by >160-fold. As suggested in previous studies, effects range values should be referenced with caution: the relevant sediment quality guidelines have been criticized for low accuracy (overestimating toxicity), relatively high variability (in regard to observed incidence of adverse effects), and not accounting for the effects of bioaccumulation^{38,67–69} and may also further underestimate sediment toxicity due to the exclusion of known DDT metabolites such as DDMU. Nonetheless, sediment quality guidelines provide a well-recognized metric that is commonly used for the context of sediment toxicity and clearly demonstrate a potential for toxic effects in the majority of sediments sampled.

Stemming from our observations, several questions remain, including our contrasting findings of regional scale DDT mobilization versus local preservation and sediment burial as well as the underlying biogeochemical processes active or relict around the wastes. The variability that accompanied waste disposal practices undoubtedly contributes to these uncertainties and also to the potential impacts on the broader ecosystem. Despite the uncertainties, these findings serve as a cautionary tale for the disposal and dispersal of containerized industrial waste from even a quiescent benthic environment.

■ ASSOCIATED CONTENT

📄 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.8b05859.

Detailed description of the mapping and sampling, analytical, and DDX mass balance data and methods, images of additional barrels, maps of dumpsite location, and chemical concentrations for each depth horizon and metabolite analyzed (PDF)

Identification of compounds in sediment-core extracts (PDF)

Compound identification criteria and comparison (PDF)

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Notes

The authors declare no competing financial interest.

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