San Francisco Estuary Regional Monitoring Program for Trace Substances

Identification and Evaluation of Unidentified Organic Contaminants in the San Francisco Estuary

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EXECUTIVE SUMMARY

In the mid-1960s, contaminants routinely detected but not characterized in fish from the San Francisco Estuary included the PCBs, which are currently among the legacy pollutants of greatest concern. More recently, the widely used insecticide diazinon was identified after first appearing as an "unknown" organic compound in water samples. Effective sustainable management of the San Francisco Estuary requires that these contaminants are identified before they become legacies for future generations. The objectives of this special study were the following: 1) to conduct the first comprehensive assessment of the identities, concentrations, and distributions of as many as possible of the previously unknown organic contaminants present in the San Francisco Estuary, 2) to link newly identified contaminants to known or suspected adverse impacts such as toxicity and bioaccumulation, and 3) to target potential problem contaminants for monitoring. This special study is significant because it is the first attempt at "surveillance monitoring" for organic contaminants, and it makes the regulatory system more "proactive" in anticipating potential problem contaminants in the San Francisco Estuary. It is also similar to a recent reconnaissance study conducted by the U.S. Geological Survey (USGS) that specifically targeted pharmaceuticals, hormones, and other organic wastewater contaminants in U.S. streams (Kolpin *et al.*, 2002). However, in this study, which is broader in scope, effort was placed on finding recently identified aquatic contaminants already cited in the scientific literature, such as those targeted in the USGS study, and new aquatic contaminants.

The surveillance monitoring was accomplished by analyzing the archived gas chromatographic-mass spectrometric (GC-MS) electronic data from environmental samples collected by the Regional Monitoring Program for Trace Substances (RMP). The GC-MS electronic data contain the signals of many previously unidentified natural and anthropogenic organic compounds. The information provided in these electronic data is sufficient to characterize natural organic matter and anthropogenic contaminants by compound classes and to provide other clues to their identification.

The samples that were analyzed included water from the Sacramento and San Joaquin Rivers (1993, 1994), water (1993, 1994) and sediments (1993) from the San Francisco Estuary, and a treated wastewater final effluent (1997, 1998) from a publicly owned treatment works (POTW) located in the South Bay (Palo Alto, CA). Data collected from various sampling sites along the spine of the San Francisco Estuary (at the RMP Dumbarton Bridge, Yerba Buena Island, San Pablo Bay, and Grizzly Bay stations) were specifically selected to obtain a broad understanding of the distributions and abundances of organic compounds throughout the Estuary.

The results show the presence of both natural (e.g., terrestrial and marine plants) and anthropogenic (e.g., petroleum and synthetics) organic compounds and their alteration products in environmental samples. There also remained some compounds that could not be identified and assigned to either a natural or anthropogenic origin due to the following reasons: 1) the compounds were new, alteration products or secondary metabolites that were difficult to identify based on interpretation of their mass spectral signatures alone, and because mass spectra for such compounds were not always

available from the scientific literature for making comparisons, and 2) the coelution of low level (at or slightly above the GC-MS chromatographic baseline or noise level) compounds with high level compounds resulted in mass spectra that contained fragment ions (pieces of the parent molecule) from both compounds such that the identification of the low level compound, or sometimes both, could not be made due to the fragment ion interferences in the co-eluted mixture.

Most of the identifications were assigned to the major resolved peaks in the GC-MS chromatograms (see Appendices) that were derived from either natural or anthropogenic sources. Still, much of the effort focused on identifying the synthetic compounds that were present at low levels in the samples. The low-level synthetic compounds, although not necessarily shown as labeled peaks in the GC-MS chromatograms, were included in Table 2. The compounds that were reported represent only a fraction of the total pool of compounds that are present in the San Francisco Estuary. The distributions and abundances of natural and anthropogenic organic compounds in the Estuary can vary both spatially and temporally (i.e., seasonal) due to changes in the natural fluid flow regime (e.g., tidal processes, storm events, etc.) and in loading rates of wastewater and stormwater discharges.

It was necessary to identify and report the occurrences of natural compounds from terrestrial (vascular plants) and marine (phytoplankton and zooplankton) sources in this study because they were generally present as major organic components in the GC-MS chromatograms (see Appendices 1-31). In comparison with anthropogenic compounds, natural compounds were also more widely distributed and contributed more to the total organic matter in the environmental samples. The lipid fractions (solvent-soluble organic matter) of San Francisco Estuary water and sediment samples and Sacramento and San Joaquin river water samples were composed predominantly of homologous compound series of n-alkanes, n-alkenes, n-alkanals, n-alkanols, n-alkanoic acids, and n-alkanones. These compound groups are derived mainly from epicuticular waxes of terrestrial plants. Other natural compound groups that were identified include the diterpenoids from gymnosperm (conifer) resins and waxes, and isoprenoids and steroids (phytosterols) from plant internal lipid components. Thermal alteration (burning) products of these compounds such as retene were also found. Zooplankton contributed wax esters and fatty acids, while algae contributed unsaturated and saturated n-alkanes to the natural organic matter pool.

Anthropogenic organic compounds may derive from a variety of sources and can enter the Estuary through various pathways (e.g., atmospheric deposition, sewage treatment plant effluent discharge, boating activities, agricultural and urban runoff, and soil erosion). The anthropogenic organic compounds in the environmental samples that were detected at ng/L levels (parts per trillion) or higher and are of concern include the nitro and polycyclic musks used as fragrances (musk ketone, musk xylene, Galaxolide™, and Tonalide™), p-nonylphenol used in the production of non-ionic surfactants, phenols used as antioxidants and preservatives (butylated hydroxy toluene and butylated hydroxy anisole), polybrominated diphenyl ethers (PBDEs) used as flame retardants, phthalates used as plasticizers in industrial polymers (di-n-butylphthalate, butylbenzyl phthalate, and bis(2-ethylhexyl)phthalate), triphenylphosphate used as a flame retardant and plasticizer, pesticides (benfluralin and trifluralin), and petroleum (n-alkanes, biomarkers, and PAH).

In comparison to the median concentrations reported in the USGS study (Kolpin *et al*., 2002), the concentrations of the similar compounds in this study were mostly lower (Table 19). Also, the nitro and polycyclic musks and some other compounds that were identified in this study were previously reported in a special report on pharmaceutical and personal care products found in the environment (Daughton and Ternes, 1999).

Evidence from the scientific literature suggests that some of the synthetic organic compounds and their biological metabolites may induce toxicity, have the potential to adversely affect normal endocrine system functions depending on exposure dosage and bioavailability, and accumulate in marine biota (e.g., planktivorous fish, crabs, and bivalves) and in higher food chain consumers (e.g., predatory fish, birds, marine mammals, and humans). The major sources of these synthetic chemical classes into the aquatic environment is primarily through the discharge of treated wastewater effluents, urban and agricultural runoff, soil erosion, and atmospheric deposition.

Petroleum hydrocarbon pollution and contamination of the environment, especially of water bodies such as the San Francisco Estuary, are of environmental concern. Although careful measures can be taken to deter petroleum contamination in water bodies, small amounts of uncombusted lubricating oil and gasoline are often unavoidably introduced into water during operation, repairs, fueling, and pumping of bilge from boat engine compartments. Equally important are the contributions from atmospheric deposition of vehicular combustion emissions and unburned petroleum (e.g., lubricating oil) from street runoff. Fossil fuels were identified as the most dominant source of solvent-extractable organic matter in most of the Estuary sediment samples and as a minor component in some water samples. The primary fossil fuel derived organic components identified in sediment and water samples included the n-alkanes, isoprenoids (pristane and phytane), tricyclic terpanes, hopanes, steranes, diasteranes, polycyclic aromatic hydrocarbons (PAH), and the unresolved complex mixture (UCM), which is composed of highly branched and cyclic hydrocarbons. Our results show that San Francisco Estuary sediments are an environmental sink for crude oil, refined petroleum products, and their combustion alteration derivatives. In the early years of the RMP the total petroleum hydrocarbon concentrations for sediments were reported but this information was dropped in the later years.

The most abundant organic constituents that are often identified in GC-MS chromatograms of environmental samples are not necessarily the most important ones. For example, a compound present at a low level near the chromatographic baseline that has potential to bioaccumulate or induce a significant toxic effect at very low dose concentrations, can pose a greater threat to aquatic biota than a compound that is non-bioaccumulative, non-toxic, and present at a high level. Water and sediments are composed of heterogeneous organic mixtures and attempts to identify a single organic compound in the mixture that is responsible for an observed toxic effect to aquatic biota is very difficult and requires the use of sophisticated laboratory based toxicological tests.

Although organic contaminant maximum concentrations during the water (1993, 1994) and sediment (1993) sampling seasons were well below the reported LC_{50} value for some aquatic species, their present concentrations and adverse ecosystem effects (if any) in the San Francisco Estuary still remain unknown. As a “proactive” effort, several of the newly identified synthetic organic compounds of concern were recommended for

screening in the 2002 RMP trace organics monitoring program because of their potential to persist in the environment, bioaccumulate in tissues, and induce toxicity. These compounds were the polybrominated diphenyl ethers (PBDEs), phthalates, nitro and polycyclic musks, p-nonylphenol, and triphenylphosphate. The samples reported in this study were collected at far-shore sampling locations along the spine of the Estuary. These organic contaminants are expected to reach concentrations that are much higher at near-shore sampling locations. It is also expected that they will be widely distributed in the San Francisco Estuary, Sacramento and San Joaquin River water, sediments, and in fish and shellfish tissues.

Information collected from the scientific literature that addresses the environmental distributions, characteristics, occurrences, and toxicity of individual compounds and compound classes of concern that were identified in this study has been provided. Still, more definitive information and research on compound behavior (e.g. partitioning between environmental mediums and biological tissue), bioavailability (e.g., biochemical reactivity and toxicity) and fate (e.g., bioaccumulation, biodegradation, burial in sediments, etc.) in the San Francisco Estuary is needed in order to link these newly identified contaminants to any suspected adverse impacts.

I. INTRODUCTION

The purpose of this investigation was to conduct the first comprehensive assessment of the identities, concentrations, and distributions of as many as possible of the previously unidentified organic contaminants present in water and sediment samples collected from the San Francisco Estuary, water samples collected from the Sacramento and San Joaquin Rivers, and wastewater effluent samples collected from a publicly owned treatment works (POTW) in the South Bay. This was accomplished by analyzing the archived gas chromatographic-mass spectrometric (GC-MS) electronic data collected by the San Francisco Estuary Regional Monitoring Program for Trace Substances (RMP).

Electronic outputs compiled by GC-MS are used in the RMP to measure selected organic contaminants in environmental samples (water and sediment) and biological tissues. These outputs also contain the signals of many unidentified contaminants. The information contained in these data is often sufficient to characterize contaminants by compound classes and to provide other clues to their identification. By using the electronic data, we can determine the environmental concentrations and distributions of trace organic contaminants in the San Francisco Estuary during the recent past. This information, when coupled with toxicological data, can then be used to make preliminary assessments of the need to regulate their use.

The study included the quantification of unknown organic compounds present in water, treated wastewater effluent, and sediment samples. This was accomplished through the following activities: 1) assembling and archiving data submitted by the contract laboratories, 2) searching the literature for newly identified (previously unidentified) compounds, and producing a list of other candidate compounds that might be found, 3) identifying as many as possible of the peaks in the GC-MS data and connecting the peaks with these newly identified compounds, 4) searching the literature for adverse ecological or human health effects of compounds found in the local data, and 5) disseminating information from this study in a final report.

Because of the enormous inventory of anthropogenic chemicals in current use not yet monitored, we sought to minimize the duplication of effort in their identification. Therefore, the recent scientific literature was searched for current- or recent-use compounds identified using chemical methods identical or similar to those used in the RMP analyses. For example, the mass spectrometric data of known organic pollutants were collected from the published literature and the National Institute of Standards and Technology (NIST) Chemistry WebBook and used to identify unknowns by comparison.

The scientific literature was searched for potential ecological or human health effects of newly identified compounds found in the archived GC-MS data. Literature concentrations associated with observable effects were then compared with concentrations found in local samples. This work occurred concurrently to compound identification and quantification.

II. METHODS

A. WATER SAMPLING AND ANALYSIS

Polyurethane foam plugs were Soxhlet extracted for three days with acetone/hexane (2:1) followed by three days extraction with methanol and then sealed in Teflon™ bags for transport to the field. POTW wastewaters were collected in 1997 and 1998, consisting of both grab samples extracted *in situ* with polyurethane foam and 4-liter composite samples collected over a 24-hour period that were liquid-liquid extracted with methylene chloride (CH_2Cl_2). Water data analyzed in this study were from RMP samples collected in 1993 and 1994 (SFEI, 1994, 1995). After arriving at a sampling site, the vessel was anchored and the engine was turned off. Whole water was sampled at approximately 1 m below the water surface through Teflon™ tubing that was attached to an aluminum pole that was oriented upcurrent from the vessel and upwind from equipment and personnel by pumping through a Teflon™ impeller pump. Water was pumped first through a glass fiber filter (0.3-0.45 µm nominal pore size) to obtain a separate particulate fraction and then through four polyurethane foam plugs mounted in series to avoid water by-passing the plugs. Samples consisted of approximately 100 liters. Caution was taken to minimize contamination at all levels of sample collection and handling. The entire trace organics sampling system was thoroughly rinsed with methanol prior to water sampling.

Foam plugs and filters were each Soxhlet extracted first with acetone to include all water and then with hexane; extracts were then combined. At this stage an internal standard mixture was added consisting of deuterated PAH and decachlorobiphenyl (PCB 209) (1993 and 1994 samples) or pentachloronitrobenzene and PCBs 103 and 207 (Palo Alto wastewater samples). Water and acetone were removed with separatory funnels, and the hexane was reduced to a volume of about 1 ml by rotary evaporation followed by evaporation under a gentle stream of purified nitrogen. Cleanup was accomplished by Florisil™ column chromatography into non-polar (F1), semi-polar (F2), and polar (F3) fractions. All organic solvents used were of analytical grade. The fractions were then each concentrated by rotary evaporation followed by evaporation under purified nitrogen to initial volumes of about 0.4 ml for analysis by electron capture gas chromatography and gas chromatography-mass spectrometry (GC-MS).

B. SEDIMENT SAMPLING AND ANALYSIS

Sediment samples were collected using a modified Van Veen grab with a surface area of 0.1 m^2. The grab was made of stainless steel, and the jaws and doors were coated with dykon to improve chemical inertness. All scoops, buckets, and stirrers used to collect and composite sediments were also constructed of Teflon™ or stainless steel coated with dykon. When the sampler was on deck, the top 5 cm of sediment was scooped from each of two replicate grabs and mixed in a bucket to provide a single composite sample for each station. Sediment samples were freeze-dried, mixed with kiln-fired sodium sulfate, and then Soxhlet extracted with methylene chloride for a minimum of 6 hours. Deuterated PAH and PCB 209 were added as surrogate recovery standards prior to extraction to account for methodological analyte losses. After solvent exchange

into hexane, treatment was the same as described above for water extracts. The internal standard, 1,2,3,5-tetrachloro-4,6-dimethyl-benzene, was added to the final extracts just prior to GC-MS analysis.

C. INSTRUMENTAL ANALYSIS

A 1 µl splitless injection was analyzed on a Saturn II GC-MS equipped with an 8100 autosampler using electron impact (70 eV) in full spectrum ion monitoring mode. The GC was equipped with a fused silica capillary column coated with DB-5 (30 m x 250 µm i.d.; 0.25 µm film thickness, J&W Scientific, Folsom, CA). The temperature program of the GC oven was as follows: isothermal at 100 °C for 5 min, 4 °C/min to 280 °C, held isothermal at 280 °C for 15 min. Helium was used as the carrier gas. Organic compounds were identified in the GC-MS data by their characteristic mass fragmentation patterns.

D. DATA ANALYSIS

The electronic GC-MS full spectrum data were generated from 1993 and 1994 water and sediment samples. Wastewater effluent samples collected in 1997 and 1998 from a POTW in the South Bay were also analyzed for trace organics. The GC-MS data were screened using Saturn GC-MS Workstation software (Varian, Inc.) with the National Institute of Standards and Technology NIST 92 and NIST 98 mass spectral reference libraries. When organic compound identifications were not possible with the mass spectral reference libraries, identifications were made by comparison with literature mass spectra and by interpretation of mass spectrometric fragmentation patterns.

The high number of environmental samples previously collected made it necessary to select representative water and sediment samples from different segments of the San Francisco Estuary. The RMP sampling sites that were analyzed included Dumbarton Bridge, Yerba Buena Island, San Pablo Bay, Grizzly Bay, Sacramento River (Rio Vista, CA), San Joaquin River (Manteca, CA), and a POTW in the South Bay (Fig. 1). The initial screening of GC-MS chromatograms showed the presence of many organic compounds in the environmental samples as evidenced by numerous peaks. Attempts were made to identify all of the organic components in every sample by screening every resolved peak present above the baseline in a GC-MS chromatogram. Once a positive compound identification was made, either by a mass spectral reference library match, comparison with the published literature, or by manual interpretation of the mass spectrum, the newly identified compound was then screened as a target analyte in other samples.

Quantification was based on comparison of peak abundance to the known response of internal standards. The organic analyte concentrations were corrected for surrogate standard losses prior to reporting.

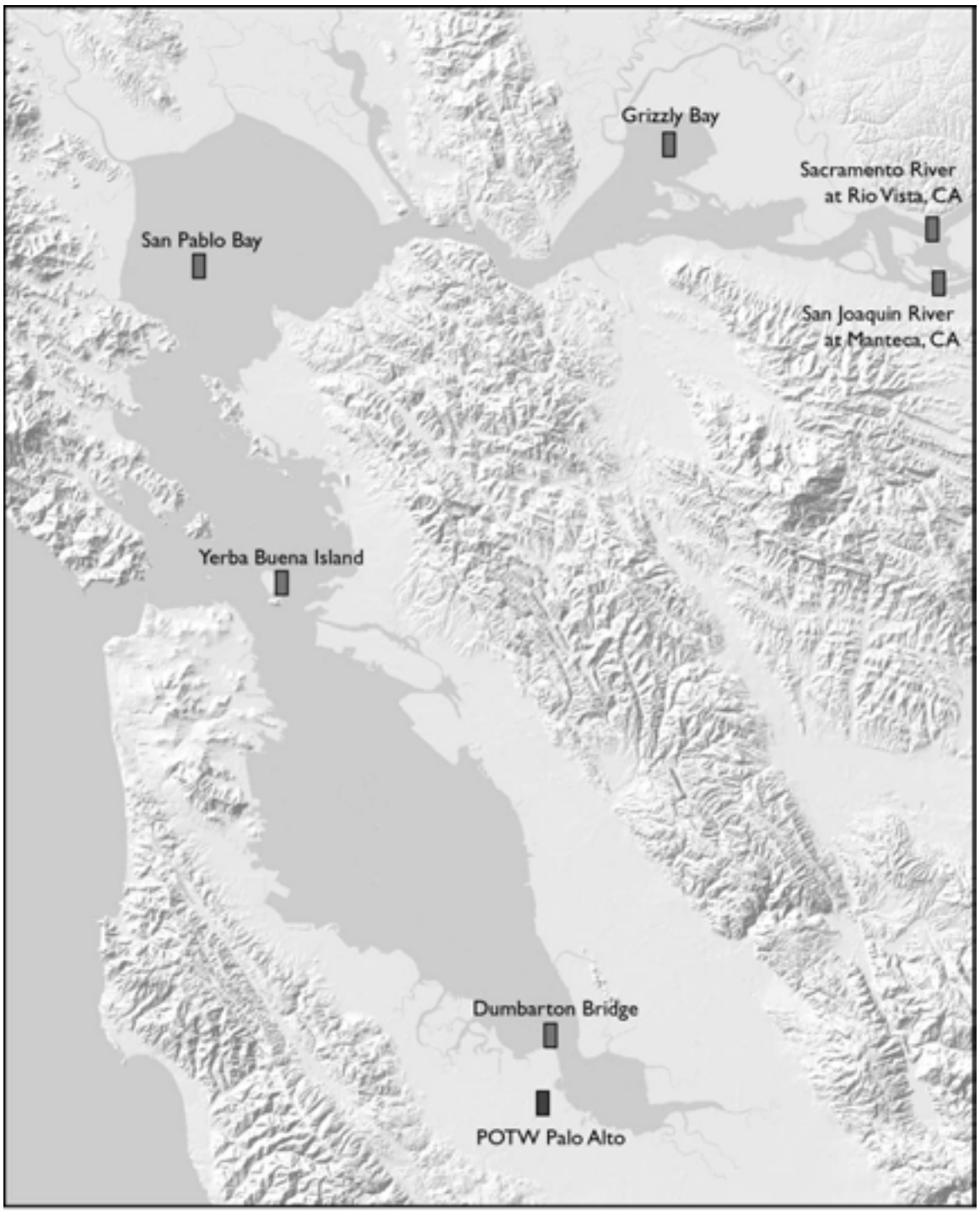

Figure 1. Locations of sampling sites.

E. METHOD LIMITATIONS

It is important to mention that the sample preparation, enrichment, cleanup, fractionation, and analytical methodology that were employed for the Estuary samples may have excluded an unknown portion of organic compounds. For example, methylene chloride (CH_2Cl_2) was used as the primary organic solvent for extracting the lipid soluble organic compounds in sediments, leaving within the sample matrices the non-lipid soluble or medium to high range polar organic constituents. As a second example, polar organic compounds such as acids, phenols, and some alcohols and amines often chromatograph poorly. Therefore, to improve their elution by chromatography sample extracts containing polar compounds are usually derivatized (e.g., acylation, alkylation, silylation, and condensation) prior to being injected into the gas chromatograph. In this study, none of the sample extracts were derivatized so some medium to high range polar compounds were lost in the GC-MS analyses. Hence, the GC-MS chromatograms show an incomplete and limited picture of the actual organic compositions for the environmental samples that were analyzed.

The surrogate standard used for the water samples was decachlorobiphenyl (PCB 209). This compound is a hydrophobic polychlorinated biphenyl (PCB) congener that is generally used as a reference recovery standard for assessing methodological losses of hydrophobic compounds (e.g., PCBs) during the sample storage, extraction, and fractionation steps. Since some of the contaminants of interest are generally more hydrophilic (e.g., phenols), their recoveries could have been much lower and the concentrations that are reported in this study could be underestimated.

The sampling program also presents several limitations on spatial and temporal scales. For instance, water and sediment samples were collected only once per year in the dry season along the spine of the Estuary at mid-bay areas (deep channels) away from shorelines. This sampling approach eliminated all the shallow water depth near-shore sites that are more heavily influenced by input of allochthonous (transported from another environment) organic matter (terrestrial and anthropogenic sources) from rivers, urban and storm water runoff, wastewater effluent discharge, soil erosion, and tidal mixing. At near-shore sites, both water and sediments are heterogeneous or mixed with respect to their organic matter compositions containing both labile (reactive) and refractory (non-reactive) organic matter. In comparison with near-shore sites, mid-bay areas receive mostly autochthonous (originate at or are close to site of deposition) organic matter from sources such as marine phytoplankton and zooplankton. The exogenous organic matter found at mid-bay sites is mostly biodegraded and refractory due to its distant transport and long residence time once released into the marine environment.

Several physical factors that can influence spatial and temporal differences in organic matter compositions between sampling sites in the Estuary include water temperature (higher surface water temperature increases photosynthesis and bacterial activity), depth (less light and colder water temperatures with increased depth), wind speed (increases water mass and sediment mixing), river flow rates (increases dilution during wet season and rainfall events), turbidity (increases suspended sediment load during wet season), sedimentation rate and texture (influences amount of particulate organic matter buried and preserved in sediments), tidal activity (causes fluctuation in fresh- and saltwater mixing zones), and light intensity (increases photosynthesis

especially in summer due to longer days). Important chemical factors include dissolved oxygen content (aerobic versus anaerobic conditions especially in sediments), pH (in fresh- and saltwater mixing zones causes flocculation of clay and other particles with increased adsorption of metals and other materials on the flocculates), nutrients (enrichment increases primary production by marine phytoplankton), and salinity (influenced by tides and freshwater inflow especially in the North Bay and Delta regions).

Finally, because of the methods that were applied, along with the fact that the Estuary is a dynamic and open system that experiences spatial and temporal variability, the data reported here present an incomplete and limited picture of the organic compositions of water and sediment in the San Francisco Estuary. However, the natural and anthropogenic compounds that were found in the samples are invaluable when they are used as "chemical tracers" to identify the major sources of organic matter input to the aquatic ecosystem.

III. RESULTS AND DISCUSSION

The GC-MS total ion current traces of the environmental and POTW effluent samples are provided in Appendices 1-31. The peaks identified in the GC-MS traces represent the major or most abundant organic components in each sample. Each sample is separated into dissolved and particulate phases to show the relative distributions and partitioning behavior of individual organic compounds between the two phases. Also, within both phases (dissolved and particulate) are the separate fractions that provide information on individual compound or group functionality and polarity: non-polar (F1), semi-polar (F2), and polar (F3). References to individual or sets of GC-MS traces provided in the Appendices section will be made throughout this report to support observations of organic compound occurrence in samples.

The results show the presence of both natural (e.g., terrestrial and marine plants) and anthropogenic (e.g., petroleum and synthetics) organic compounds and their alteration products in environmental samples. There also remained some compounds that could not be identified and assigned to either a natural or anthropogenic origin (Table 18). Most of these unknown compounds were likely alteration products (i.e., chemical, physical, and biological), or secondary metabolites (i.e., bacteria, plant, animal, and fungi) that were difficult to identify based on their mass spectral signatures alone.

A. NATURAL COMPOUNDS

It was necessary to identify and report the occurrences and distributions of natural compounds from terrestrial (vascular plants) and marine (phytoplankton and zooplankton) sources in this study because they were generally present as major organic components in the GC-MS chromatograms (see Appendices 1-31). In comparison with anthropogenic compounds, natural compounds were also more widely distributed and contributed more to the total organic matter in the environmental samples. The following describes the chemical compositions, distributions, and fate of natural organic matter found in the San Francisco Estuary.

Most natural organic matter released into the aquatic environment is degraded and only traces are usually preserved in sediments. Organic matter found in modern coastal marine sediments is typically composed of 10-15% amino acids, 5-10% carbohydrates, 3-5% lignin (Cowie and Hedges, 1992; Cowie *et al*., 1992), and less than 5% total lipid (Tissot and Welte, 1984). More than 66% of the total organic carbon (TOC) in marine sediments cannot be accounted for at the molecular level because it cannot be hydrolyzed or it has been degraded beyond chemical recognition (Hedges and Oades, 1997). In this study, the total lipid (CH_2Cl_2) soluble component that is elutable by GC accounts for <5% of the TOC that is present naturally in the marine sediment samples. The use of Florisil™ for sample fractionation and cleanup can also decrease the total extractable lipid content. Of the extractable and elutable organic mass, 40-60% could be resolved chromatographically as single compound peaks. The remainder is made up of closely eluting organic compounds that form the unresolved complex mixture (UCM) that is present as a "hump" in the GC-MS chromatograms (see Section 8: Petroleum).

Natural organic matter released into the environment (e.g., plant litter and detritus to soil surfaces, wildfire emissions to the atmosphere, and soil organic matter washed into rivers and streams) contains the chemical fingerprint of its principal vegetation source (Oros and Simoneit, 1999; Oros *et al*., 2002). The distributions and abundances of the organic compounds that make up the chemical fingerprint are strongly dependent on the vegetation source and extent of degradation from microbial and thermal (i.e., biomass burning) alteration processes (Oros and Simoneit, 2001a, 2001b). Once released into the environment, the lipids (e.g., hydrocarbons) and structural biopolymers (e.g., cellulose, hemicellulose, and lignin), in comparison with other organic compounds (e.g., protein, nucleic acid biopolymers, and polysaccharides), are mostly refractory and undergo limited microbial degradation. Thus, they can be identified in soil and sediments where they are partially degraded and preserved.

Natural compounds and their alteration (thermal and biological degradation) products were the predominant organic components in most of the San Francisco Estuary samples. The most common natural compound groups identified in the samples are listed in Table 1. These groups consisted mostly of straight-chain homologous series, isoprenoids, terpenoids, steroids (phytosterols) and wax esters. Concentrations of the natural compounds identified in the environmental samples were not determined since they pose no known threat to the health of the aquatic environment. Brief descriptions of the distributions and sources of the individual compounds and compound groups that were identified in the environmental samples are provided.

The lipid fractions (solvent soluble organic matter) of water and sediment samples were composed predominantly of homologous compound series of n-alkanes, n-alkenes, n-alkanals, n-alkanoic acids, n-alkanols, and n-alkanones that are derived mainly from plant epicuticular waxes (Kolattukudy, 1970; Oros *et al*., 1999). Other natural compound groups that were identified included the mono- and sesquiterpenoid compounds (C_{10} and C_{15}, respectively) that are derived from essential oils, and diterpenoid (C_{20}) compounds derived from conifer resin and waxes. Steroids (phytosterols) from plant internal lipid components and their alteration products were also identified in the samples.

Natural compounds in the Estuary and its tributaries may originate from a variety of sources such as phytoplankton, zooplankton, bacteria, macrophytes, zoobenthos, and

fish. Phytoplankton are the most important producers of organic matter in the aquatic environment. Within the water column, algae (e.g., diatoms and dinoflagellates) may contribute saturated and unsaturated hydrocarbons having both straight and branched chains. Algae synthesize n-alkanes in the range from C_{14}-C_{32}, where often C_{15} or C_{17} or both are the predominating n-alkanes from this aquatic plant source (Simoneit *et al*., 1980; Tissot and Welte, 1984). A homologous series of unsaturated n-alkenes were present in the particulate fractions of both river and Estuary water samples. These compounds were identified as n-$C_{17:5}$, n-$C_{19:4}$, n-$C_{19:5}$, n-$C_{21:5}$ and n-$C_{23:5}$ and have been previously attributed to derive from aquatic algal sources (Volkman *et al*., 1998) (Appendix 4).

Terrestrial vascular plants can contribute high molecular weight epicuticular waxes (i.e., lipids, on leaves and needles), terpenes (bark and tree resins), and other particles containing lipids (e.g., spores and pollen) to the aquatic environment mostly through indirect pathways (e.g., surface water runoff, soil erosion, and atmospheric deposition). Lipid compounds in aquatic systems from terrestrial higher plants have been previously characterized (Hatcher *et al*., 1982; Simoneit, 1978; Simoneit *et al*., 1980). In the Estuary and river water samples, the n-alkanes ranged from C_{25}-C_{35}, with a strong preference for the C_{27}, C_{29}, and C_{31} odd carbon numbered n-alkanes (Appendices 17-24). The n-alkanals ranged from C_{20}-C_{28} and were predominated by the even carbon numbered homologs (Appendix 2). Aliphatic alcohols (n-alkanols) ranging from C_{18} to C_{29} with C_{24} and C_{26} as the predominant n-alkanols were also relatively common (Appendix 3). These three compound groups are all major components of terrestrial higher plant epicuticular waxes (Oros *et al*., 1999). The most prominent fatty acids in the samples were generally palmitic acid (C_{16}), C_{18} monounsaturated acids, and stearic acid (C_{18}), which are basic units of plant fats, oil, glyco- and phospholipids. They were present as free fatty acids and as fatty acid methyl esters (FAMES) (Appendix 4). Esterified fatty acids in contemporary sediments have previously been associated with indigenous animals, microalgae, and bacteria (Volkman *et al*., 1998).

The biodegradation of plant detritus material in the water column results in the release of chlorophyll a and its breakdown to phaeophytin and phytol (3,7,11,15-tetramethyl-2-hexadecen-1-ol), the alkyl side chain of chlorophyll. Phytol was identified in most of the water and sediment samples (Appendix 2). Squalene**,** a triterpene, was also identified as a major natural component in most of the Estuary and river water samples (Appendix 1). Squalene is the precursor molecule in the biosynthetic pathway for steroid production.

Zooplankton and other micronekton also contribute hydrocarbon compounds to the water column, primarily by reproduction, excretion, feeding activities, and by the decomposition of detrital organic matter. Lipids from zooplankton that were identified in the Estuary samples included wax esters, which consist of long chain alcohols, range from C_{12}-C_{18}, coupled to a fatty acid, range from C_{12}-C_{18}, through an ester functional group linkage (Sargent *et al*., 1976; Appendix 12). Bacteria in the water column and in the sediments can contribute functionalized hopanoid biomarkers (e.g., hopanols, hopenes) that are pentacyclic terpenoids derived primarily from their membranes (Simoneit, 1978; Peters and Moldowan, 1993). Hopanoid compounds were identified in most of the sediment samples, however, because of the extent of their biogeochemical

alteration (present as reduced hopanes not functionalized compounds) and stereochemistry (i.e., 17α(H),21β(H) configuration, which signifies geologically mature organic matter) their major source was attributed primarily to petroleum contamination (Appendix 25; also see Section 8 on Petroleum).

The Estuary and its tributaries are also subject to aerosol fallout from spores, pollen and other natural particles such as resuspended soil detritus. Natural aerosols are normally composed of particles with adsorbed organic compounds from vegetation sources such as the high molecular weight epicuticular plant waxes, fatty acids (C_{12}-C_{30}), and terpenes (conifer resins) (Simoneit, 1989). The burning of biomass can also contribute natural and altered plant biomarker compounds through particulate matter fallout and field runoff. The presence of retene, an alteration product from burning of conifer resin compounds, in some of the San Francisco Estuary water samples indicates that biomass burning of conifer wood is also a source of organic matter to the aquatic environment (Ramdahl, 1983; Standley and Simoneit, 1987, 1994) (Figure 2; Appendix 3).

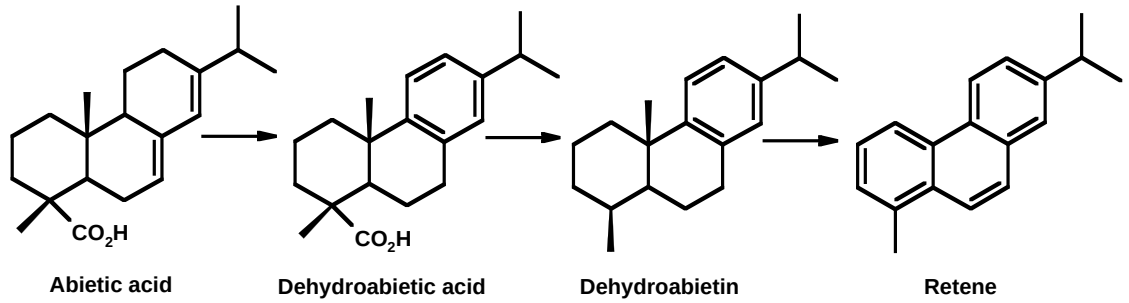

Figure 2. Alteration pathway of retene formation from abietic acid.

B. ANTHROPOGENIC COMPOUNDS

Anthropogenic organic compounds may derive from a variety of sources and can enter the Estuary through various pathways (e.g., atmospheric deposition, POTW and industrial wastewater effluent discharge, boating activities, agricultural and urban runoff, and soil erosion, etc.). The anthropogenic organic compounds in the environmental samples that were detected at ng/L levels (parts per trillion) or higher and are of concern include the nitro and polycyclic musks used as fragrances (musk ketone, musk xylene, Galaxolide™, and Tonalide™), p-nonylphenol used in the production of non-ionic surfactants, phenols used as antioxidants and preservatives (butylated hydroxy toluene and butylated hydroxy anisole), polybrominated diphenyl ethers (PBDEs) used as flame retardants, phthalates used as plasticizers in industrial polymers (di-n-butylphthalate, butylbenzyl phthalate, and bis(2-ethylhexyl)phthalate), triphenylphosphate used as a flame retardant and plasticizer, pesticides (benfluralin and trifluralin), and petroleum (n-alkanes, biomarkers, and PAH). Several of these compounds were also recently identified in a similar reconnaissance study conducted by the USGS that targeted pharmaceuticals, hormones, and other organic wastewater contaminants in U.S. streams (Kolpin *et al.*, 2002). In comparison, the concentrations of these compounds in this study were mostly lower than the median concentrations reported in the USGS study (Table 19). Also, the

nitro and polycyclic musks and some others that were identified in this study have previously been reported in a comprehensive report on pharmaceutical and personal care products found in the environment (Daughton and Ternes, 1999).

Recent evidence in the scientific literature has shown that several of the identified synthetic organic compounds and their metabolites can induce toxicity and bioaccumulate in marine biota (e.g., planktivorous fish, crabs, and bivalves) and in higher food chain consumers (e.g., predatory fish, birds, marine mammals, and humans). Some studies have specifically identified p-nonylphenol, phthalates, polybrominated diphenyl ethers, and triphenylphosphate as compounds that exhibit hormonal activity with the potential to disrupt normal endocrine system functions depending on exposure dosage and bioavailability. The major sources of these synthetic chemical classes into the aquatic environment is primarily through the discharge of treated wastewater effluents, urban and agricultural runoff, soil erosion, and atmospheric deposition.

The most common anthropogenic compounds identified in this study are listed in Table 2. Table 2 also provides their concentrations, chemical information, location of highest abundance, and when available, the lowest LC_{50} values (lethal concentration with 50% mortality) of the most sensitive aquatic indicator species. Tables 3-8 show the concentrations and distributions of select synthetic compounds of concern in the environmental samples. These compounds are of concern because of their ability to persist in the environment, bioaccumulate in tissue, and induce toxicity. Their chemical structures, common uses, and brief descriptions of their toxic effects are provided in Tables 9-17.

General information collected from the published literature on the characteristics, occurrence, and toxicology of the important individual compounds and compound classes of concern that were identified in this study is included in Sections 1-8 below. This background information is useful for assessing environmental risk, making comparisons with similar studies, and planning future studies to better understand the sources, transport pathways, fate, and effects of these compounds in the aquatic environment.

1. Nitro and Polycyclic Musks

Regional Distributions

The distributions and concentrations of the nitro and polycyclic musk compounds that were identified as major components in some of the regional samples are provided in Tables 2-8. Their chemical structures, common uses, and toxic effects are provided in Table 9. The most common nitro musk compounds were identified as musk ambrette, musk ketone, and musk xylene (Table 2). Musk ketone, the most abundant nitro musk compound, showed a maximum concentration in a San Pablo Bay water sample (12 ng/L). Musk ketone was not detected in river water and San Francisco Estuary sediment samples. The microbial alteration of musk xylene by the nitro-reductase enzymatic pathway yields 4-amino-musk xylene as a secondary metabolic product (Rimkus, 1999). This compound was identified in several samples with its highest concentration (1 ng/L) in Dumbarton Bridge water (Appendix 1). The most common polycyclic musk compounds were identified as Galaxolide™, Phantolide™, Tonalide™, and Traseolide™

(Table 2). These compounds, which are similar in structure, were identified by their characteristic mass spectrum and elution order in the GC-MS chromatograms as previously reported in the literature (Osemwengie and Steinberg, 2001). Galaxolide™, the most abundant polycyclic musk compound, had a highest abundance in a Dumbarton Bridge water sample (227 ng/L, Appendix 1). Galaxolide™ was found in San Francisco Estuary water samples but not in sediment samples. Galaxolide™, but not musk ketone, was detected as a contaminant in some of the blank samples, however, its concentration was generally much lower than that found in the environmental samples.

The nitro and polycyclic musk compounds are used as fragrances in cosmetics and personal care products. Based on the scientific literature, the major source of these compounds into aquatic environments is POTW wastewater effluent that is discharged directly into receiving waters. Fromme *et al*. (2001) reported mean concentrations for Galaxolide™ in surface water samples collected in Germany from areas that were mildly and heavily impacted by sewage as 70 ng/L and 1590 ng/L, respectively. In comparison, the San Francisco Estuary (maximum concentration at 227 ng/L) and the Sacramento (maximum concentration at 0.4 ng/L) and San Joaquin (maximum concentration at 1 ng/L) Rivers during the 1993 and 1994 sampling periods were only mildly impacted. The ability of some of these compounds to bioaccumulate and induce toxicity further increases concern over their occurrence in the Estuary. Their present impact, if any, on the aquatic ecosystem remains unknown. General information collected from the published literature on the characteristics, occurrence, toxicological effects, and threshold levels of the nitro and polycyclic musk compounds that were identified in this study is included below.

Characteristics

The ability of nitro musks to accumulate in lipids is relatively high (log K_{ow} for musk ketone is 4.9 and musk xylene is 4.2) and their biodegradability is low. They can accumulate in the environment and in biota and can also biomagnify in the food web. Several other nitro musk compounds that are used as fragrances include musk ambrette, musk moskene, and musk tibetene.

The polycyclic musk compounds are synthetic enantiomeric fragrances that are used in almost all scented household and personal care products, such as laundry detergents, perfumes, and cosmetics. At present, these compounds have a global production volume of about 6000 t/yr. After their use in household and personal care products, these compounds are released into the aquatic environment as components of treatment plant wastewater effluents (Rimkus, 1999). Several other polycyclic musk compounds that are also used as fragrances include Cashmeran™, Celestolide™, Crysolide™, and Versalide™.

Balk and Ford (1999a) conducted an environmental exposure assessment of Tonalide™ and Galaxolide™ and reported the following properties: vapor pressure 0.0682 and 0.0727 Pa; water solubility 1.25 and 1.75 mg/L; log K_{ow} 5.7 and 5.9; log K_{oc} 4.80 and 4.86; and bioconcentration factor in fish: 597 and 1584 (fresh weight), respectively. In addition, the synthetic musk compounds were previously identified in

municipal sewage effluent using GC-MS in the full spectrum ion monitoring mode (Osemwengie and Steinberg, 2001).

Toxicology and Thresholds

Musk xylene induces cytochrome P450 enzymes in rats, particularly those in the CYP1A family. In mice, musk xylene causes generalized hepatic changes. Musk xylene is also a potent inhibitor of the CYP2B enzymes (Scientific Committee on Food, 1997). The metabolism of nitro musk compounds by rats and humans can lead to the formation of genotoxic intermediates, aromatic amines, since the nitro groups are reduced to amino groups (Scientific Committee on Food, 1997).

Steinberg *et al*. (1999) reported that a single high dose of Tonalide™ in rats caused acute hepatic damage characterized by single cell necrosis, inflammation, liver parenchymal cell swelling, and increased cytoplasmic condensates in hepatocytes. At the ultrastructural level, they reported disorganization of rough endoplasmic reticula and mitochondria, and focal cytolysis. Steinberg and co-investigators also found that Tonalide™ is not genotoxic, and does not induce peroxisome proliferation and cytochrome P450 enzymes.

Versalide™ had been used in the fragrance industry since the 1950s. In the mid-1970s it was discovered that it was severely neurotoxic and caused the internal organs of mice to turn blue (Spencer *et al*., 1979). It has since been withdrawn from commercial use (Dictionary of Toxicology, 1983). Musk ambrette is also neurotoxic and its use in cosmetic products has been banned in the European Union. Furthermore, it has been found to be mutagenic in *Salmonella typhimurium* following its metabolic activation (Dictionary of Toxicology, 1983).

Tas and Plassche (1996) reported that musk ketone, like musk xylene, is a strong inducer of cytochrome P450 enzymes. Carlsson *et al*. (2000b) reported that musk ketone negatively affected reproduction and the early life-stage survival of zebrafish. They reported reduced body weight, length, reduced liver- and gonad-somatic index, and a dose-dependent reduction in fecundity. Musk ketone exposure increased early life-stage mortality and reduced the median survival time. Carlsson *et al*. (2000b) also reported a no observed effect concentration (NOEC) threshold at 10 µg/L and a lowest observed effect concentration (LOEC) threshold at 33 µg/L.

Balk and Ford (1999b) conducted 72 h toxicity tests on algae (*Pseudokirchneriella subcapitata*) and reported NOECs of 374 µg/L for Tonalide™ and 201 µg/L for Galaxolide™. They also conducted a 21-day reproductive tests with daphnids (*Daphnia magna*) and reported NOECs of 196 µg/L for Tonalide™ and 111 µg/L for Galaxolide™. Additionally, in 21-day growth tests with bluegill sunfish (*Lepomis macrochirus*), the NOECs were reported as 67 µg/L for Tonalide™ and 68 µg/L for Galaxolide™. In 35-day early life stage tests with fathead minnows (*Pimephales promelas*), the NOECs were 35 µg/L for Tonalide™ and 68 µg/L for Galaxolide™.

Occurrence

Water: Winkler *et al*. (2000) analyzed Elbe River water samples for Galaxolide™, Tonalide™, Celestolide™, and musk ketone. They reported that Celestolide™ and musk ketone concentrations were below the detection limits (14 and 22 ng/L, respectively), Tonalide™ was below the limit of quantification (22 ng/L), and Galaxolide™ present at 117 ng/L. Rimkus *et al*. (1999) reported that the monoamino metabolites, 4-NH_2-musk xylene and 2-NH_2-musk ketone, were the dominant compounds in Elbe River water samples.

Heberer *et al*. (1999) reported nitro and aromatic musk compounds in surface water samples collected around Berlin. Galaxolide™ and Tonalide™ concentrations in receiving waters reached the µg/L level. Heberer *et al*. (1999) also reported that in the Wuhle, a brook almost totally consisting of sewage effluents, maximum concentrations were 12.5 µg/L for Galaxolide™ and 6.8 µg/L for Tonalide™. The musk compounds Celestolide™ and musk ketone were also reported to occur in most samples, however, at low concentrations (Heberer *et al*., 1999). Fromme *et al*. (2001) found mean concentrations for Galaxolide™ in surface water samples that were collected from areas that were heavily and mildly impacted by sewage as 1.59 µg/L and 0.07 µg/L, respectively.

Sediment: Fromme *et al*. (2001) reported mean concentrations for Galaxolide™ in sediment samples collected from areas that were heavily and mildly impacted by sewage as 0.92 mg/kg dry weight and <0.02 mg/kg dry weight, respectively.

Wastewater: Simonich *et al*. (2000) identified musk ketone, musk xylene, Galaxolide™, and Tonalide™ in secondarily treated wastewater samples. They reported the following final effluent concentrations: musk ketone (99 ng/L), musk xylene (5 ng/L), Galaxolide™ (1170 ng/L), and Tonalide™ (1180 ng/L). The removal efficiencies for these compounds by secondary wastewater treatment were reported as 83, 99, 92, and 89%, respectively. Fromme *et al*. (2001) reported a mean concentration of 6.85 µg/L (maximum: 13.3 µg/L) for Galaxolide™ at a sewage outfall. In comparison, these reported concentrations are much higher than the levels found in the POTW wastewater sample analyzed in this study: Galaxolide™ (177 ng/L) and musk ketone (4 ng/L).

Rimkus (1999) identified the monoamino microbial metabolites of musk xylene and musk ketone, in sewage effluent (4-NH_2-musk xylene, 34 ng/L; 2-NH_2-musk ketone, 250 ng/L) and in fish (tenches) collected from a sewage pond (4-NH_2-musk xylene, 3600 µg/kg lipid). He also found maximum Galaxolide™ and Tonalide™ concentrations in sewage pond water samples at 6 µg/L and 4.4 µg/L, respectively.

Sewage Sludge: Herren and Berset (2000) reported the presence of nitro- and polycyclic musk compounds in sewage sludge samples. Musk ketone and musk xylene were the major nitro musk compounds in predominantly domestic sewage sludges, found at low µg/kg dry matter. The polycyclic musks were present in both domestic and industrial sludges at levels up to 12 mg/kg dry matter. Galaxolide™ and Tonalide™ were identified as the major polycyclic musks found in the sludges. Herren and Berset (2000) also reported that amino metabolites of the nitro musks, 4-amino-musk xylene, NH_2-

musk moskene, and NH_2-musk ketone were present in sewage sludges at concentrations higher than their parent precursor compounds.

Rimkus (1999) conducted a study on musk compounds in sewage sludge and found maximum Galaxolide™ and Tonalide™ concentrations at 63 mg/kg dry matter and 34 mg/kg dry matter, respectively.

Aquatic Biota: Gatermann *et al*. (1999) analyzed tissue samples from Canadian aquatic fauna such as lobster, winter flounder, American eel, lake trout, clams, and mussels, for nitro and polycyclic musk compounds. They reported that samples from densely populated areas, Halifax and the industrialized Miramachi Estuary, showed relatively high concentrations of musk ketone (maximum levels: mussels 2200 µg/kg lipid; winter flounder muscle 2700 µg/kg lipid; clams 17700 µg/kg lipid) and Galaxolide™ (maximum levels: mussels 1700 µg/kg lipid; winter flounder 40 µg/kg lipid; clams 3000 µg/kg lipid), while samples from a sparsely populated area, Cap-Pele, exhibited lower levels of musk compounds (musk ketone maximum level: 130 µg/kg lipid; Galaxolide™ maximum level: 16 µg/kg lipid). Most of the samples were reported to contain relatively low concentrations of musk xylene and Tonalide™. Furthermore, Gatermann *et al*. (1999) showed that in Western Europe, the concentrations of Galaxolide™ and Tonalide™ in fish exceed those of nitro musk compounds by one to three orders of magnitude.

Gatermann *et al*. (1999) reported musk xylene (50 µg/kg lipid) and musk ketone (64 µg/kg lipid) in a pollock (*Pollachius virens*) lipid sample from the Halifax area. Hajšlová *et al*. (1998) conducted a study in the Czech Republic of fish (breams, perches, and chubs) collected at the Elbe River. They reported that Galaxolide™ and Tonalide™ concentrations were higher than those of nitro musks with the highest concentrations of Tonalide™ and Galaxolide™ at 3194 µg/g and 1289 µg/g fat, respectively. The high concentrations were reported to derive from a detergent producing factory located upstream of the sampling site.

The maximum concentrations of musk xylene, musk ketone, and musk ambrette in farmed fish (mainly trout) and fish originating from rivers were reported as 90, 68 and 1 µg/kg fresh weight, respectively (Scientific Committee on Food, 1997). Fromme *et al*. (2001) reported mean bioconcentration factors for Galaxolide™ and Tonalide™ transfer from water to eel at 3504 and 5017, respectively. Franke *et al*. (1999) also reported the presence of the polycyclic musks in different aquatic species.

Fromme *et al*. (2001) reported mean concentrations for Galaxolide™ in eel samples collected from areas that were heavily and mildly impacted by sewage as 1513 µg/kg fat (in the edible portion) and 52 µg/kg fat, respectively. Rimkus (1999) conducted a study on musk compounds in fish collected from sewage ponds and reported maximum Galaxolide™ and Tonalide™ concentrations at 159 mg/kg lipid and 58 mg/kg lipid, respectively. Rimkus *et al*. (1999) found that the secondary metabolite of musk xylene, 4-NH_2-musk xylene, was the major monoamino metabolite in aquatic biota.

Humans: Rimkus and Wolf (1996) analyzed 14 human adipose tissue and 5 human milk samples for polycyclic musk compounds. They reported that Galaxolide™ ranged from 16-189 µg/kg fat and Tonalide™ ranged from 8-58 µg/kg fat. Muller *et al*.

(1996) also identified nitro and polycyclic musk compounds in 15 human adipose tissue samples collected in Switzerland. They reported that musk xylene and Galaxolide™ concentrations reached up to 288 µg/kg lipid and 171 µg/kg lipid, respectively.

Zehringer and Herrmann (2001) analyzed 53 human milk samples from the region of Basel, Switzerland for PCBs, pyrethrins, pyrethroids, and musk fragrances. They reported that while the PCBs showed a decreasing trend in mean concentrations since 1980, Galaxolide™ (73 µg/kg fat) and Tonalide™ (74 µg/kg fat) were detectable in almost every sample. Pyrethrin and pyrethroid insecticides were detected at low concentrations between 0.03 and 0.46 mg/kg fat. Human milk was reported to contain up to 1.2 mg/kg and 0.2 mg/kg fat of musk xylene and musk ketone, respectively (Scientific Committee on Food, 1997). Absorbtion through skin has been identified as a pathway of musk compound entry in humans (Bronaugh *et al*., 1998).

2. p-Nonylphenol

Regional Distributions

Technical grade p-nonylphenol (NP) consists of a mixture of isomers with differently branched structures of the nonyl side chain (Wheeler *et al.*, 1997). The multiple isomers are produced during its synthesis or through environmental degradation (Fig. 3a). Hereafter, we refer to the isomeric mixture as p-nonylphenol. A characteristic GC-MS fragmentogram of a NP branched isomer (structure shown) is provided as a reference (Fig. 3b). The distributions and concentrations of NP in regional samples are provided in Tables 2-8. Its characteristic chemical structure, common uses, and toxic effects are provided in Table 10.

NP was detected as a minor trace organic component in wastewater effluent (42 ng/L) and in Sacramento (19 ng/L, Appendix 21) and San Joaquin (5 ng/L) river water samples. NP was not detected in San Francisco Estuary water and sediment samples. NP was detected as a contaminant in the blank samples from wastewater (0.03 ng/L), however, its concentration was much lower than that found in the POTW wastewater effluent sample (42 ng/L).

Similar environmental studies have also shown NP as an organic component in water samples. Bennie *et al*. (1997) conducted a survey of inshore stations in the lower Great Lakes and St. Lawrence River and reported NP concentrations at less than 1 µg/L in water. In a study by Naylor *et al*. (1992), NP was identified in 30% of all water samples at concentrations ranging from 200 to 640 ng/L. The USGS study on U.S. streams reported a NP maximum concentration at 40 µg/L and a median concentration at 0.8 µg/L (Kolpin *et al*., 2002). These NP concentrations were much higher than the NP levels that were found in the San Francisco Estuary (see Tables 2 and 19). NP levels of up to 1600 µg/L were reported in industrial effluents (Shackelford *et al*., 1983). Garrison and Hill (1972) reported that NP concentrations in river water downstream from a discharge ranged from 2 to 3,000 µg/L, and Ferguson *et al*. (2001) reported NP concentrations at 4 to 416 ng/L in Jamaica Bay, New York. In comparison to these sites, the concentrations of NP found in the 1994 Sacramento and San Joaquin river (5-19 ng/L) water samples are low.

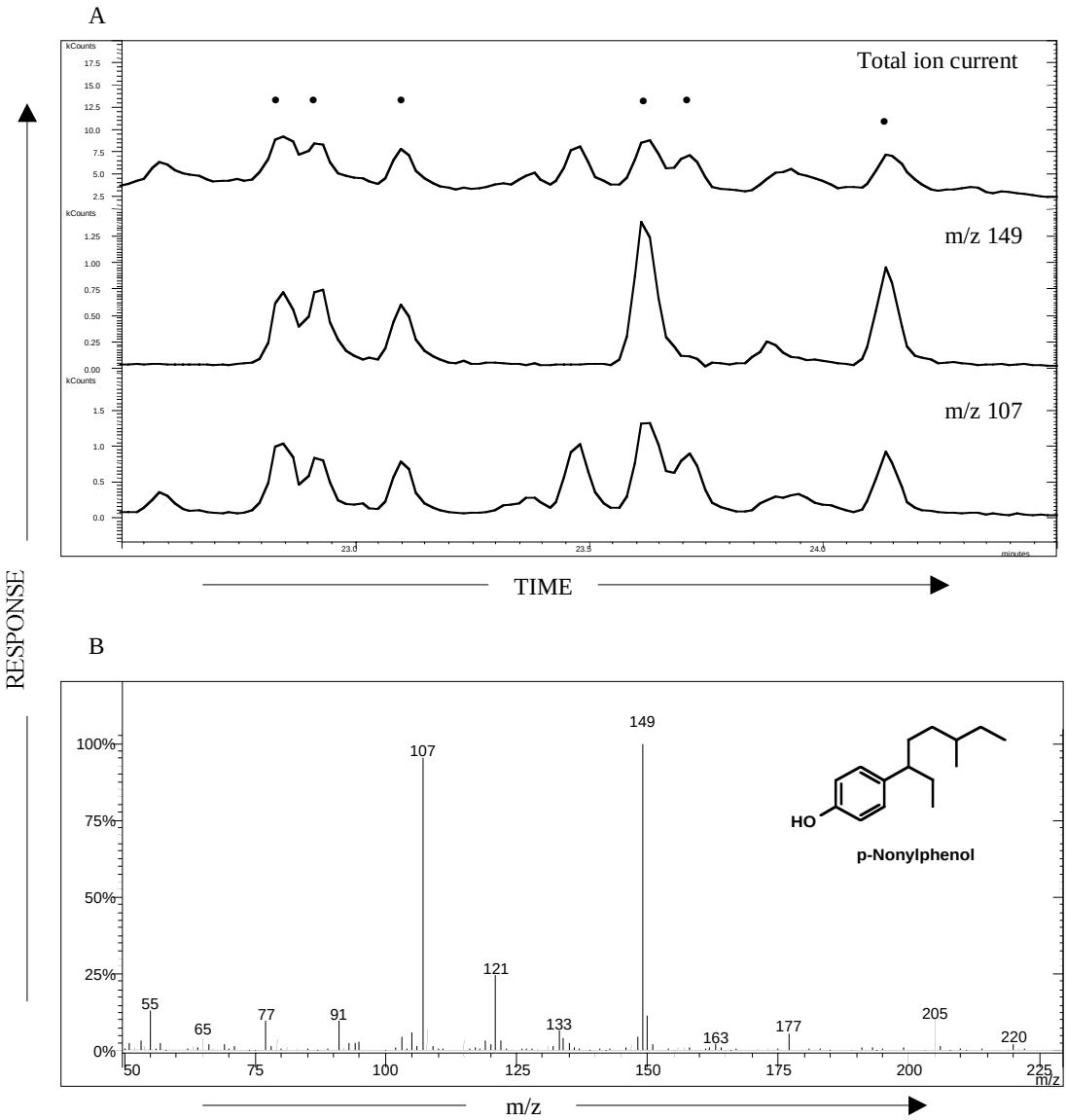

Figure 3. GC-MS traces of a 1994 river water sample from Sacramento River, Rio Vista, showing p-nonylphenol isomers: A) fraction 2 total ion current trace and key fragment ions m/z 149 and 107, and B) mass fragmentogram of a p-nonylphenol isomer. Closed dots • are p-nonylphenol isomers. Abbreviation: m/z = mass/charge.

NP is primarily used as a precursor in the manufacture of non-ionic surfactants. NP is also a degradation product of alkylphenol ethoxylates that are used in household detergents, pesticide formulations, and other applications (Fig. 4). The ability of NP to bioaccumulate and potential to adversely affect normal endocrine system functions depending and dosage and bioavailability further increases concern over its occurrence in the aquatic ecosystem. Its present impact on the aquatic ecosystem, if any, remains unknown. General information collected from the published literature on the characteristics, occurrence, toxicological effects, and threshold levels of NP is included below.

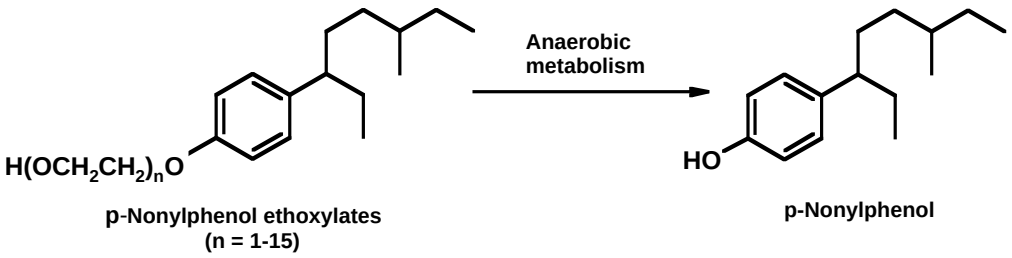

Figure 4. Alteration pathway of p-nonylphenol formation from anaerobic metabolism of p-nonylphenol ethyoxylates.

Characteristics

NP is a viscous, colorless, lipophilic liquid that has bioaccumulative properties (Shiraishi, 1989). NP is a mixture of branched nonyl-chain and ring substituted isomers. The industrial synthetic process produces three major NP isomers: 2-(4-hydroxyphenyl)-nonane, 3-(4-hydroxyphenyl)-nonane, and 4-(4-hydroxyphenyl)-nonane (Meldahl *et al*., 1996). NPs are used as intermediates in the production of nonylphenol ethoxylates (NPEs) and other alkylphenyl ethoxylates (APEs). These ethoxylated compounds are used as components of household detergents, lubricants, antistatic agents, emulsifiers for agrichemicals, antioxidants for rubber and plastics, and as oil-additives (Reed, 1978). The NPs are also degradation products of APEs. NPs were identified as ubiquitous contaminants in food ranging from 0.1-19.4 µg/kg regardless of the fat content of the foodstuff (Guenther *et al*., 2002). NPs are ubiquitous in environmental samples such as surface waters and aquatic sediments (Naylor *et al*., 1992). Bennett and Metcalfe (2000) showed that sewage treatment plant discharge is the major source of APE degradation products in the lower Great Lakes basin. Bennett and Metcalfe (2000) also stated that APE degradation products have the potential to concentrate in sediments, water, and biota that are near sewage treatment plants.

NP has the potential to bioaccumulate in aquatic organisms. Wahlberg *et al*. (1990) conducted a study in the Glatt River (Europe) and reported that NP, nonylphenol monoethoxylates (NP1E), and nonylphenol diethoxylates (NP2E) were present in aquatic plants and fish at mg/kg and µg/kg concentrations, respectively. Wahlberg *et al*. (1990) reported that these compounds also bioaccumulated in marine mussels (*Mytilus edulis*) that were caged at several industrial sites in Europe. The bioaccumulation factors for NP ranged from <100 (McLeese *et al*., 1981) to >1000 (Ekelund *et al*., 1990). Bioconcentration factors of NP in fathead minnows ranged from 245-380 (Snyder *et al*., 2001).

Ekelund *et al*. (1993) reported that free NP biodegradation in the aquatic environment is only about 0.06% per day, especially in the absence of sediments. The results of a freshwater study conducted by Heinis *et al*. (1999) showed that the loss of NP from the water column was rapid (6-22 days) and that degradation of sediment-associated NP was not detected. Shang *et al*. (1999) found that nonylphenol ethoxylates (NPEs) and their metabolites (i.e., NP) persisted in marine sediments with a reported half-life of 60 years. Dachs *et al*. (1999) and Van Ry *et al*. (2000) both reported that volatilization also

played a significant role in the fate of alkylphenol ethoxylate (APEO) metabolites, including NP, that are released into the near-shore marine environment.

Toxicology and Thresholds

Several studies have shown that NP is bioaccumulated (Ekelund *et al*., 1990), estrogenic (Armstrong and Kingsbury, 1979; Gray and Metcalfe, 1997), and highly toxic to fish and other species (McLeese *et al*., 1980; McLeese *et al*., 1981; Granmo *et al*., 1989; U.S. EPA, 1996). Soto *et al*. (1991) reported that NP induced cell proliferation and activated the progesterone receptor in human estrogen-sensitive MCF-7 breast tumor cells. It also triggered mitotic activity in rat endometrium (Soto *et al*., 1991). The estrogenic properties of NP are potentially harmful to exposed humans and the environment (Maguire, 1999). NP can also act as an agonist for the androgen receptor (Hill, 1985).

The induction of vitellogenin (a precursor of egg yolk) synthesis in male fish is used as a common indicator of environmental exposure to estrogenic compounds (Arcand-Hoy *et al*., 1998). Madsen *et al*. (1997) administered six injections of 17ß-estradiol or NP into one-year-old Atlantic salmon (*Salmo salar*) over 30 days and reported that all the treatments resulted in activated vitellogenisis, inhibited smoltification, and impaired saltwater tolerance. Tabata *et al*. (2001) reported that female specific proteins were induced in medaka exposed to 0.1 µg/L of NP. Abnormal gonad development was detected when medaka were exposed to 100 µg/L of NP, while abnormal anal fin (female-like) development was observed in males exposed to the same concentration (Tabata *et al*., 2001). Leblanc *et al*. (1999) conducted developmental toxicity tests on daphnids and showed that NP interfered with the metabolic elimination of testosterone.

Lussier *et al*. (2000) measured the acute toxicity of NP to early life stages of several saltwater invertebrates and fish. They reported 96 h LC_{50} threshold concentrations as the following- Invertebrates: mysid *Americamysis bahia*, formerly *Mysidopsis bahia*, (60.6 µg/L), stone crab *Dyspanopeus sayi* (>195 µg/L), American lobster *Homarus americanus* (71 µg/L), amphipod *Leptocheirus plumulosus* (61.6 µg/L), coot clam *Mulinia lateralis* (37.9 µg/L, 48 h LC_{50}), grass shrimp *Paleomonetes vulgaris* (5904 µg/L); Fish: winter flounder *Pleuronectes americanus* (17 µg/L), sheepshead minnow *Cyprinodon variegatus* (142 µg/L), and inland silverside *Menidia beryllina* (70 µg/L). Lussier *et al*. (2000) also reported that the threshold concentrations were well within the range of NP concentrations found in industrial effluents and sewage sludge. They further identified that mixing zones, areas where effluents enter receiving waters, could become concentrated with enough NP to harm aquatic biota. The U.S. EPA adopted 12.4 µg/L as the national water quality criteria guideline for NP in saltwater (U.S. EPA, 1993). The concentrations of NP during the sampling period in this study were well below this guideline. At this time, it is not known if present day levels of NP in the San Francisco Estuary are exceeding the guideline.

Occurrence

Sediment: The degradation products of APEs (e.g., NP) are relatively hydrophobic and readily adsorb to particulate material. Bennett and Metcalfe (1998) reported mean concentrations of NP and octylphenol (OP) of up to 37.8 and 23.7 µg/g, respectively, in sediments near sewage treatment plants and industrial wastewater discharges in the Great Lakes. Bennie *et al.* (1997) reported NP in sediment at 72 µg/g in the Hamilton Harbor in western Lake Ontario. Bennett and Metcalfe (2000) also tested sediments in the Hamilton Harbor near a sewage treatment plant discharge and reported NP at a concentration of 110 µg/g. In a survey of U.S. river sediments, Naylor *et al.* (1992) reported that NP was present in 70% of the samples tested at concentrations ranging from 10 to 3000 ng/g. Khim *et al.* (2001) reported NP maximum concentrations at 1040 ng/g (15000 ng/g TOC) in sediments from the highly industrialized region of Ulsan Bay, Korea. The NP concentrations reported were greater at locations near wastewater discharge sites. Ferguson *et al.* (2001) reported NP concentrations that ranged from 7-13700 ng/g of sediment in Jamaica Bay, New York.

Aquatic Biota: Bennett and Metcalfe (2000) analyzed tissues from freshwater mussels (*Elliptio complanata*) that were deployed for 2 weeks in a sewage treatment plant discharge in the Detroit River. They reported NP, NP1E, and NP2E concentrations in tissues at 500, 90, and 50 µg/kg wet weight, respectively. Bennett and Metcalfe (2000) stated that the low lipid content of the mussels resulted in the low reported NP concentrations. Shiraishi *et al.* (1989) analyzed tissue from carp collected at the Trenton Channel of the Detroit River near a chemical plant that manufactured alkylphenols. They reported that fish tissues contained p-tert-pentylphenol (a p-nonylphenol isomer) at 40 µg/g fat, which was higher than that found in sediment.

3. Phenols and Related Compounds

Regional Distributions

The distributions and concentrations of the phenols and related compounds that were identified as major components in some of the regional samples are provided in Tables 2-8. Their chemical structures, common uses, and toxic effects are provided in Table 11. Various phenolic compounds were identified in the samples. The antioxidant 2,6-di-tert-butyl-4-methyl-phenol or butylated hydroxy toluene (BHT) was often identified as the most abundant organic component in water (maximum concentration at 2.5 µg/L, Appendix 7), river water (Appendix 17), and wastewater (Appendix 31) samples. It was present in both the dissolved and particulate organic fractions of samples. It was also a common contaminant in some of the blank samples, often present at concentrations comparable to those found in the environmental samples. Thus, the BHT data should be used with caution.

BHT is an antioxidant for food, animal feed, petroleum products, synthetic rubbers, plastics, animal and vegetable oils, and soaps. It is also used as an antiskinning agent in paints and inks. The compound 3,5-di-tert-butyl-4-hydroxy anisole or butylated hydroxy anisole (BHA), which is generally used as an antioxidant and preservative in food, cosmetics, pharmaceuticals, rubber and petroleum products, was also identified,

however only as a minor component in the POTW wastewater effluent sample. The concentration of BHT in the environmental samples did not exceed the lowest LC_{50} value for the most sensitive indicator aquatic species (Table 2). Several of the phenolic compounds identified were also recently reported in the USGS study that targeted pharmaceuticals, hormones, and other organic wastewater contaminants in U.S. streams (Kolpin *et al*., 2002). In comparison, the maximum concentration of BHT reported in that study (0.1 µg/L) was lower than the maximum concentration found in this study (2.5 µg/L) (see Table 19).

Alteration and Reaction Products

Several alteration products of BHT were identified in the samples and their distributions and concentrations were as follows: 4-methylene-2,6-di-tert-butyl-2,5-cyclohexadienone (58 ng/L in San Pablo Bay water), 2,6-di-tert-butyl-p-benzoquinone (1 ng/L in Dumbarton Bridge water), 2,6-di-tert-butyl-4-hydroxy-4-methyl-2,5-cyclohexadien-1-one (78 ng/L in Yerba Buena Island water), 2,6-di-tert-butyl-1-methoxy-4-ethyl-benzene (0.02 ng/L in San Pablo Bay water), and 2,6-di-tert-butyl-4-(methoxymethyl)-phenol (4 ng/L in Sacramento River) (Table 2). These compounds were present in both the dissolved and particulate organic fractions. These BHT alteration (oxidation) products have been previously confirmed by mass spectrometry (Brumley *et al*., 1989).

BHT was also shown to react with cyclohexene and amylene, which are antioxidant and preservative compounds that are both commonly added to the organic solvent methylene chloride. The reaction products were identified as 2,6-di-tert-butyl-4-cyclohexyl-phenol, 2,6-di-tert-butyl-4-(2,3-dimethyl-but-2-enyl)-phenol, and 2,6-di-tert-butyl-4-(2,3-dimethyl-3-hydroxy-butyl)-phenol (Table 2). These reaction products were only identified in water samples collected from San Pablo Bay, Grizzly Bay, and the Sacramento River. Because the water samples collected in this study were not extracted using methylene chloride but with acetone/hexane (2:1) and methanol, these compounds are not suspected as procedural contamination artifacts. They were found as contaminants in water samples from the North Bay region and in the Sacramento River. Their sources into the San Francisco Estuary remain unknown.

Several other phenols and related compounds that were identified include 2,6-di-tert-butyl-4-(1-methyl-1-phenylethyl)-phenol, 2,4-bis(1-methy-1-phenylethyl)-phenol, 2,4-bis(1-methyl-1-phenylethyl)-6-tert-butyl-phenol, and 2,4,6-tris(1-methyl-1-phenylethyl)-phenol (Table 2). These compounds are possibly antioxidants, antioxidant alteration products, or by-products of antioxidant synthesis. They were present in many of the environmental samples as major components.

The phenolic compounds and their alteration products have not been shown to cause adverse effects on the aquatic ecosystem, but they have not been studied in detail. They were present as major components in the GC-MS traces of most of the samples. Further research to identify the characteristics, occurrence, toxicological effects, and threshold levels of the phenols and related compounds that were identified in this study should be pursued.

4. Polybrominated Diphenyl Ethers

Regional Distributions

The distributions and concentrations of the polybrominated diphenyl ether (PBDE) compounds that were identified in the regional samples are provided in Tables 2-8. Their chemical structures, common uses, and toxic effects are provided in Table 12. PBDE compounds were identified in the environmental samples by their characteristic mass fragmentation patterns and retention times (Fig. 5). The GC-MS fragmentograms of tetrabromo diphenyl ether and pentabromo diphenyl ether are provided as references (Fig. 6). The following fragment and parent molecular ions were used to screen for PBDE compounds: diBDE, 328; triBDE, 248 and 408; tetraBDE, 326 and 486; pentaBDE, 404 and 564; and hexaBDE, 482 and 642.

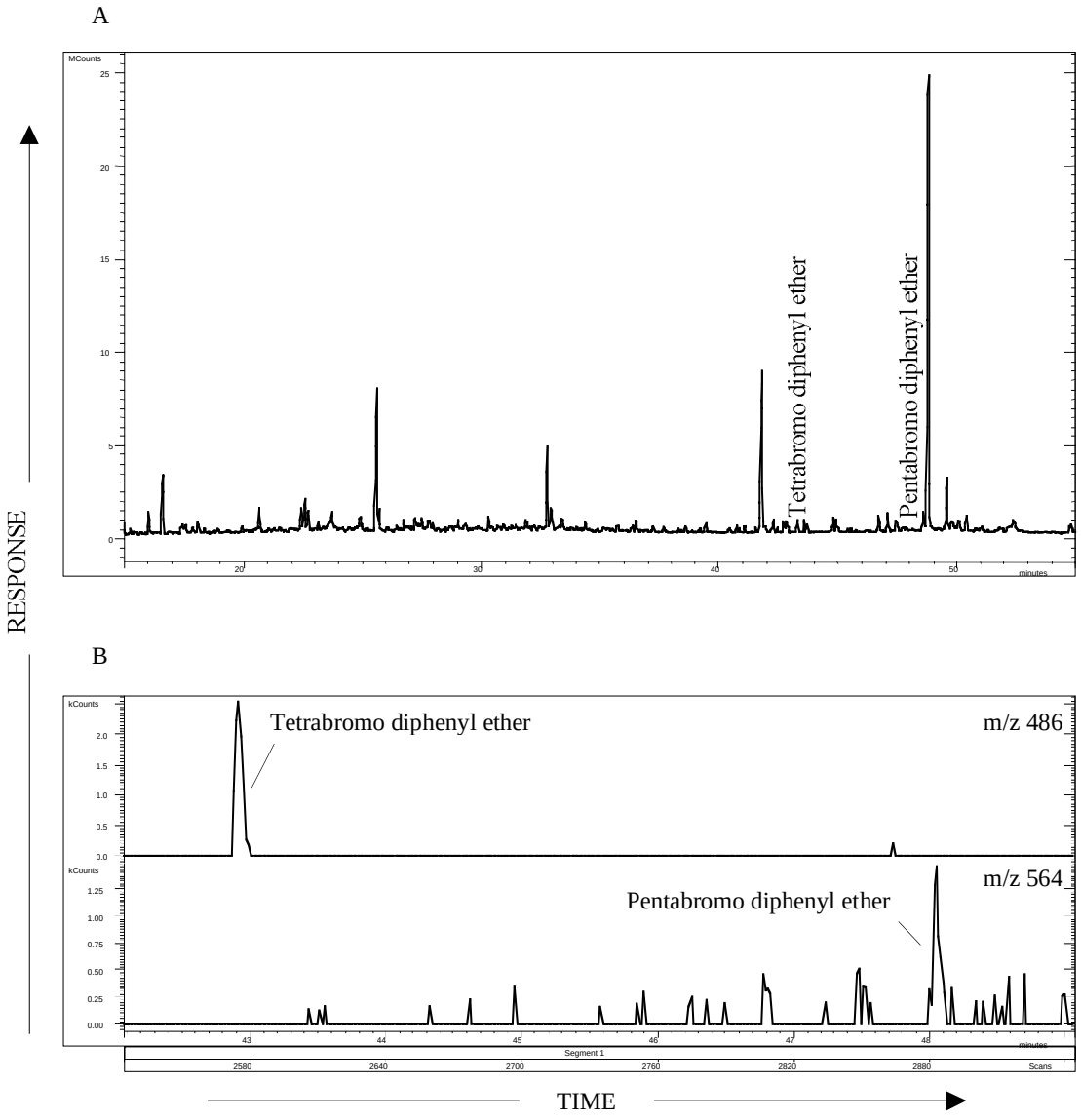

Figure 5. GC-MS traces of a 1993 water sample from San Pablo Bay showing polybrominated diphenyl ether (PBDE) compounds: A) total ion current trace of fraction 2, and B) tetrabromo diphenyl ether and pentabromo diphenyl ether (detected in data of A by the key molecular ions m/z 486 and 564, respectively).

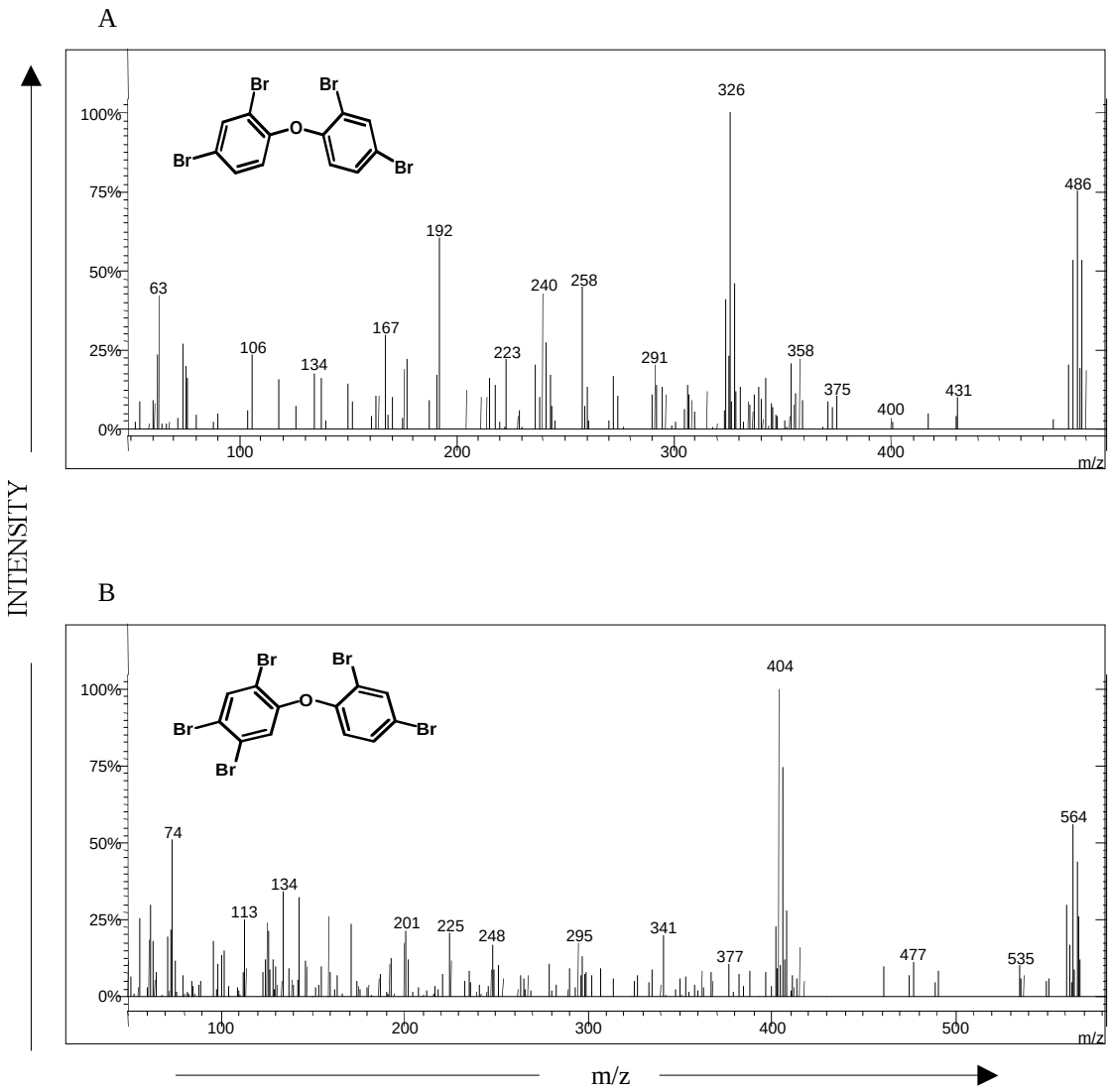

Figure 6. Mass spectra of polybrominated diphenyl ether (PBDE) compounds in a 1993 water sample from San Pablo Bay: A) tetrabromo diphenyl ether (key ions at 326 and 486), and B) pentabromo diphenyl ether (key ions at 404 and 564). Abbreviation: m/z = mass/charge.

PBDEs were identified in 1994 water samples collected from the Sacramento (tetraBDE at 5 ng/L, pentaBDE at 9 ng/L, hexaBDE at 2 ng/L; Table 7, Appendix 21) and San Joaquin (tetraBDE at 4 ng/L, pentaBDE at 14 ng/L, hexaBDE at 2 ng/L; Table 7, Appendix 23) Rivers. PBDEs were also identified in water samples from Dumbarton Bridge (tetraBDE at 3 pg/L; Table 3), Yerba Buena Island (tetraBDE at 32 pg/L; Table 6), and San Pablo Bay (tetraBDE at 10 pg/L, pentaBDE at 20 pg/L; Table 3; Fig. 5), and in wastewater effluent (diBDE at 56 pg/L, tetraBDE at 198 pg/L, pentaBDE at 27 pg/L; Table 8). Both tetraBDE and pentaBDE were identified in the 1994 water blank sample (Table 6) but not in the 1993 water blank sample (Table 3). The presence of PBDEs in the 1994 water blank sample (tetraBDE at 0.1 ng/L, pentaBDE at 0.2 ng/L) suggests that the tetraBDE observed in the 1994 Yerba Buena Island water sample (tetraBDE at 32 pg/L) was likely due to sample contamination since the tetraBDE concentration in the blank sample for that year is higher. The tetraBDE and pentaBDE concentrations found

in the 1994 water blank samples were less than the concentrations found in the Sacramento and San Joaquin River water samples. HexaBDE was not found in the water blank samples.

Polyurethane foam (PUF) plugs used for collecting the dissolved organic compounds in water might have been a possible source of contamination since PBDEs are often added to foam products as flame retardant chemicals. However, pre-sampling preparation included cleanup and extraction of sampling filters and foam plugs with solvent mixtures that should have lowered and even eliminated PBDEs from this source, had they been present, to below instrumental detection limits in the samples. Atmospheric deposition has been reported as a potential source of PBDE contamination (Strandberg *et al*., 2001).

PBDEs are primarily used as flame retardants in household and industrial products. They are also used in many polyurethane foam products. The tendency of PBDE compounds to persist once released into the environment, bioaccumulate, and potential to adversely affect normal endocrine system functions depending on dose and bioavailability, further increases concern over their occurrence in the Estuary. Their present impact, if any, on the aquatic ecosystem remains unknown. General information collected from the published literature on the characteristics, occurrence, toxicological effects, and threshold levels of the PBDE compounds that were identified in this study is included below.

Characteristics

The PBDE compounds are structurally similar to PCBs, however the PBDEs are generally more polar because they contain oxygen. Up to 209 PBDE congeners are possible, all within 10 homolog groups (mono- to decaBDE). Their solubility in water is low (0.0009 µg/L (20 ºC) for pentaBDE) and they are lipophilic. PBDEs have been shown to have a relatively high binding affinity to particles and a tendency to accumulate in sediments (IPCS, 1994; Sellstroem, 1996, 1999; Sellstroem *et al*., 1998).

The PBDEs are generally used as flame retardants in ready-made plastic products, polymers, resins and their substrates, electronic devices, building materials, and textiles. Three commercial products identified as Deca-, Octa-, and Penta-BDE compose the brominated flame retardant group known as PBDEs (Hardy, 2002). Municipal waste disposal is often the source of these compounds into the environment, along with incineration, leaching, and volatilization. Once released into the environment these compounds are persistent (Darnerud *et al*., 2001). The occurrence of PBDEs and other brominated flame retardants in the environment has been thoroughly reviewed (de Witt, 2002). In addition, a special issue of the journal *Chemosphere* (February 2002) that focuses entirely on analytical methods, environmental levels, physical properties, sources, and fate of brominated flame retardants in the environment was recently published.

Toxicology and Thresholds

PBDEs have been shown to bioaccumulate and biomagnify (Meerts *et al*., 2001). In toxicity studies of mice exposed to PBDEs, the toxic effects included hepatotoxicity,

embryotoxicity, estrogenicity, thyroid effects, and maternal toxicity during gestation (Meerts *et al*., 2001). PBDE congeners have been shown to act as agonists of both Er^{α} and $Er^{ß}$ estrogen receptors (Meerts *et al*., 2001). Similar to the PCBs and polybrominated biphenyls (PBBs), the PBDEs exhibit dioxin-like Ah-receptor-mediated induction of cytochrome P450 1A1 and 1A2 drug metabolizing and carcinogen activating enzymes (Meerts *et al*., 2001).

IPCS (1994) reported that pentaBDEs were more toxic than octa- and decaBDEs following oral administration (oral LD_{50} in rats 0.5-5 g/kg). Immunotoxicity following BDE-47 exposure (18 mg/kg/day) was also observed in mice, where the splenocyte numbers decreased (Darnerud *et al*., 2001). PBDEs also target the developing central nervous system. Darnerud *et al*. (2001) exposed neonatal mice to a single oral dose of BDE-47 (10.5 mg/kg body weight) or BDE-99 (12 mg/kg body weight) on postnatal day 10 (period of rapid brain growth and development) and reported permanent impairment of spontaneous motor behavior when the mice reached adulthood. BDE-99 was also reported to induce adverse affects on mouse learning and memory functions (Darnerud *et al*., 2001). Meerts *et al*. (2001) reported that BDE-47 induced a synergistic effect with technical preparations of PCBs in decreasing T_4 (tetraiodothyronin) thyroid hormone levels (Meerts *et al*., 2001). Alterations in thyroid homeostasis can result in permanent neurobehavorial defects (Darnerud *et al*, 2001; Meerts *et al*., 2001).

Darnerud *et al*. (2001) reported a LOEC threshold for PBDEs (mainly pentaBDE) in mice of 1 mg/kg/day (based on thyroid hormone effects). The NOEC for fetal effects in mice was reported at <2 to 15 mg/kg/day for octa- and pentaBDEs.

Occurrence

Sediment: PBDEs were first detected in sediment cores dated at 1940 and since the late 1970s their levels have increased exponentially (Nylund *et al*., 1992). Deca-, octa-, hexa-, penta-, and tetraBDEs were identified in river, estuarine, and marine sediment samples from Japan (Environmental Agency, Japan, 1991). DecaBDE was found at concentrations ranging from <25-11,600 µg/kg dry weight, while the range for the other congeners was from below the detection limit to 70 µg/kg sediment dry weight (Environmental Agency, Japan, 1991).

Sewage Sludge: Biosolid samples collected before land application from sites in Virginia, Maryland, New York, and California were analyzed and found to contain high levels of pentaBDE at 1100-2290 µg/kg dry weight and decaBDE (BDE-209) at 85-4890 µg/kg dry weight (Hale *et al*., 2001a).

Air: Air samples collected from 1997 through 1999 from urban, rural and remote sites located around the Great Lakes region showed PBDE concentrations ranging from 5 to 50 pg/m^3. Among the PBDE congeners, BDE-47 accounted for 50-65% of the total mass and BDE-99 for 35-40% (Strandberg, *et al*., 2001). De Witt (1999) reported PBDEs in air samples from Sweden ranging from 1-8 pg/m^3. Sjödin *et al*. (2001) reported that PBDE compounds were emitted into the indoor work environment of a plant that recycled and dismantled computer products. The PBDEs were present primarily in the particle-associated phase and not in the vapor phase. In a separate study conducted in that same

plant, the serum concentrations of workers were reported as significantly higher than that of a control group (Sjödin *et al*., 1999). Air resuspension of PBDE-laden particles represents another pathway by which these compounds can be transported and deposited into the aquatic environment.

Aquatic Organisms: Andersson and Blomkvist (1981) conducted a study of the Swedish river, Viskan, which received effluent water from textile factories, and reported maximum levels of PBDEs in fish of 27 mg/kg of lipid in muscle and 110 mg/kg of lipid in liver. The authors reported that penta- and tetraBDEs were more bioavailable than fully brominated BDE-209. Hale *et al*. (2001b) reported that PBDEs were present in muscle tissues of fish collected at 133 sites in the Roanoke and Dan River watersheds in Virginia, USA. They found that BDE-47 was the most abundant PBDE congener detectable in 89% of samples. Over 50% of the fish examined were reported to contain >100 µg/kg of lipid of BDE-47. Hale *et al*. (2001b) also reported that muscle tissues from carp (*Cyprinus carpio*) collected from the Hyco River contained the highest total PBDE concentration at 47.9 mg/kg of lipid (1140 µg/kg wet weight). Akutsu *et al*. (2001) reported finding PBDEs in eel, flounder, gray mullet, horse mackerel, red sea bream, sea bass, and yellowtail from the Inland Sea of Seto, Japan. The most abundant PBDE congener was BDE-47, with grey mullet (a mud-feeder) and yellowtail (a predatory and fatty fish) showing the highest concentrations in their tissues (38 and 8.1 µg/kg of lipid, respectively).

Alaee *et al*. (1999) identified tetra- to hexaBDE congeners in pilot whales of the Faroe Islands at levels ranging from 1000-3000 µg/kg lipid. BDE-47 and BDE-99 were reported to account for 70% of the total PBDEs that were identified. Bioaccumulated PBDE concentrations showed an age-related increase in Baltic herring (Strandman *et al*., 1999). Darnerud *et al*. (2001) reported that the higher brominated hepta- to decaBDEs do not bioaccumulate to a significant degree. Bioconcentration factors of <4 for BDE-209, <2 for octaBDE, <4 for heptaBDE, and <4 for hexaBDE were determined in studies of carp that were exposed for 8 weeks (CBC, 1982).

Burreau *et al*. (1997) reported an inverse relationship between the uptake efficiency and the number of bromine atoms when tetra (BDE-47), penta (BDE-99), and hexa (BDE-153) congeners were exposed to pike. The uptake efficiency of BDE-47 was over 90% and reported as the highest of all studied organohalogens (Burreau *et al*., 1997).

PBDE levels in fish from the Great Lakes were analyzed in separate studies. Alaee *et al*. (1999) reported total PBDE levels of 135-545 µg/kg lipid in Great Lakes lake trout, and Asplund *et al*. (1999) reported PBDEs at 3000 µg/kg lipid in Lake Michigan steelhead trout. Luross *et al*. (2002) reported mean concentrations of total PBDEs in lake trout from the Great Lakes: Lake Ontario 434 µg/kg lipid, Lake Superior 392 µg/kg lipid, Lake Huron 251 µg/kg lipid, and Lake Erie 117 µg/kg lipid. The three dominant PBDE congeners detected were BDE-47 (57%), BDE-99 (15%), BDE-100 (8%), which share the same 2,2',4,4' substitution pattern.

Manchester-Neesvig *et al*. (2001) analyzed tissue from coho and chinook salmon (*Oncorhynchus kisutch* and *O. tshawytscha*) caught in Lake Michigan tributaries in 1996. Six PBDE congeners were detected, and the average concentration of the sum of PBDE congeners was 80.1 µg/kg wet weight or 2440 µg/kg of lipid. BDE-49, the most abundant

congener, had an average concentration of 52.1 µg/kg wet weight or 1590 µg/kg of lipid. The rank order of concentrations of these congeners was similar to that present in commercially available PBDE mixtures. The concentrations of PBDEs were among the highest in the world for salmon in open water (Manchester-Neesvig *et al*., 2001).

Gustafsson *et al*. (1999) reported that the bioaccumulation factors (BAFs) obtained for BDE-47 and BDE-99 (1.3×10^6 and 1.4×10^6 ml/g dry weight, respectively) were higher than for PCBs of similar hydrophobicity. Also, the PBDE bioaccumulation potential is similar or higher than that of PCBs for filter feeding organisms, such as blue mussels (*Mytilus edulis*) (de Witt, 2000). In marine tissue samples collected from the coastal region of British Columbia, Canada, PBDE levels ranged from 4-2300 µg/kg lipid (Ikonomou *et al*., 2002b). Dungeness crab tissues collected at sites near industrialized and urban locations showed PBDE concentrations ranging from 200-480 µg/kg lipid, which were 80 times higher than a reference background site (4.2 µg/kg lipid). Porpoise blubber PBDEs ranged from 350-2300 µg/kg lipid, which was attributed to their higher trophic level in the marine foodweb. A separate study on porpoise blubber samples collected from England and Wales reported total PBDE concentrations ranging from not detected to 6900 µg/kg wet weight (Law *et al*., 2002).

The levels of PBDEs were shown to increase exponentially in 0-15 year old male ringed seal (*Phoca hispida)* blubber samples that were collected from subsistence hunts in the Canadian Arctic from 1981-2000 (Ikonomou *et al*., 2002a). The three most abundant PBDE congeners were identified as BDE-47, BDE-99, and BDE-100. Male seals were shown to have higher PBDE body burdens than female seals of the same age group for the same sampling years. It was suggested that female seals were decreasing their PBDE body burdens during lactation. The exponential increase of PBDEs in ringed seal blubber samples correlated well with production of the commercial Penta-BDE mixture (e.g., Bromkal 70-5DE) over the same period.

Humans: PBDEs have biomagnification potential in the food web. Darnerud *et al*. (2001) reported that tetra- and hexaBDEs are most likely the principal congeners to which humans are exposed through food consumption. BDE-47, BDE-99, and BDE-100 are regarded as the most dominant congeners present in wildlife and humans (Meerts *et al*., 2001). Meironyte *et al*. (2001) reported that the PBDE congeners BDE-47, BDE-99, and BDE-153 in human liver and adipose tissue samples collected in Stockholm, Sweden, constituted 87-96% and 84-94% of the total PBDEs, respectively. Meironyte *et al*. (1999) identified BDE-47 as the most abundant PBDE congener in human breast milk samples. They identified nine PBDE congeners in breast milk (BDE-17, BDE-28, BDE-47, BDE-66, BDE-85, BDE-99, BDE-100, BDE-153, and BDE-154). The sum of concentrations of PBDE congeners in human milk samples was reported to have increased exponentially from 0.07 µg/kg lipid in 1972 to 4.02 µg/kg lipid in 1997, with a doubling time of about 5 years (Meironyte *et al*., 1999).

Thomsen *et al*. (2002) analyzed human serum samples collected in Norway during the period of 1977 to 1999. They reported that the sum of eight brominated flame retardants, which included six PBDEs, in serum samples increased from 0.44 µg/kg lipid in 1977 to 3.3 µg/kg lipid in 1999. They also reported that serum PBDE concentrations for the different age groups were similar, except for the 0-4 year age group, which showed 1.6-3.5 times higher levels.

She *et al*. (2002) analyzed tissue samples from San Francisco Bay harbor seals and breast adipose tissue samples from 23 Bay Area women for PBDEs. The levels of PBDEs in human tissue were reported as µg/kg fat, with BDE-47, BDE-99, BDE-100, BDE-153, and BDE-154 identified as the major congeners. The average PBDE level for Bay Area women was 86 µg/kg fat, which is the highest ever reported for humans. The levels of PBDEs in harbor seal blubber ranged from µg/kg to mg/kg (average 1730 µg/kg fat), with the same PBDE congeners present as those found in human tissues (She *et al*., 2002).

5. Phthalates

Regional Distributions

The distributions and concentrations of the phthalate compounds that were identified in the regional samples are provided in Tables 2-8. Their chemical structures, common uses, and toxic effects are provided in Table 13. The phthalates identified as bis(2-ethylhexyl)adipate, bis(2-ethylhexyl)phthalate, butylbenzyl phthalate, and di-n-butylphthalate were each found in the environmental and wastewater effluent samples. The highest concentrations for bis(2-ethylhexyl)phthalate, butylbenzyl phthalate, and di-n-butylphthalate were identified in Dumbarton Bridge water at 7, 12, and 1096 ng/L, respectively (Table 2, Appendix 9). The highest concentration of bis(2-ethylhexyl)adipate was found at Yerba Buena Island (1 ng/L). The concentrations of each of the phthalates identified in the environmental samples did not exceed the lowest LC_{50} values for the most sensitive indicator aquatic species (Table 2).

Phthalates are routinely identified in environmental samples and sample blanks during organic analyses because they are now ubiquitous synthetic contaminants in the environment. They were identified here as common components in the environmental samples and as common contaminants in the sample blanks (Tables 3-8). Because pre-sampling preparation included laboratory cleanup and extraction of sampling filters and foam plugs with organic solvents, the extent of contamination in the blank samples from these two sources should have been eliminated or reduced to levels below the instrument detection limit. Phthalate contamination in the sample blanks could have occurred in the field during sampling or in the laboratory. Some materials used for storage (e.g., ice chests, plastic baggies, lid liners, and aluminum foil) of solvent cleaned solid phase extractors (e.g., foam plugs, glass fiber filters, resins, etc.) and samples can contain phthalates, thus direct surface contact with these materials should be avoided to minimize contamination.

Although the phthalate concentrations in the blank samples were usually greater than those found in the environmental samples, suggesting a contamination problem during this sampling period, the phthalates should not be overlooked as an important compound class of environmental and human health concern. General information collected from the published literature on the characteristics, occurrence, toxicological effects, and threshold levels of the phthalate compounds that were identified in this study is included below. Their distributions and concentration in present day environmental samples and ecosystem impacts, if any, remain unknown.

Characteristics

Phthalates are a class of widely used industrial compounds that are generally applied as plasticizers in industrial products such as nitrocellulose, polyvinyl acetate, polyvinyl chloride, adhesives, and coatings. They add flexibility to synthetic organic polymers. Phthalates are also used as lubricants for aerosol valves, as antifoaming agents, and skin emollients. Furthermore, these compounds are found in personal care products such as hair spray, fingernail polish, and cosmetics. They are ubiquitous in environmental samples due to their release during manufacture, use, and disposal of industrial and consumer products.

The common low molecular weight phthalate compounds are the following: dimethylphthalate, diethylphthalate, di-n-butylphthalate, and butylbenzyl phthalate. The common high molecular weight phthalates are the following: dihexylphthalate, di-(n-hexyl, n-octyl, n-decyl)phthalate, bis(2-ethylhexyl)phthalate, diisooctylphthalate, diisononylphthalate, di-(n-heptyl, n-nonyl, n-undecyl)phthalate, diisodecylphthalate, diundecylphthalate, and ditridecylphthalate.

Toxicology and Thresholds

Several detailed reviews that address the toxicology and environmental fate of phthalates have been published (Cadogan, 1999; Staples *et al.*, 1997). Data for the acute and chronic toxicities of butylbenzyl phthalate and di-n-butylphthalate on aquatic organisms such as microbes, algae, invertebrates, and fish have also been reviewed in detail (IPCS, 1997, 1999).

In an experimental study, Gray *et al*. (1999) reported that male rat reproductive development is acutely sensitive to di-n-butylphthalate and bis(2-ethylhexyl)phthalate. Di-n-butylphthalate and bis(2-ethylhexyl)phthalate exposure *in utero* changed male sexual characteristics at levels far beneath those of previous toxicological concern. Using 8-day old rats, Gray *et al*. (1999) reported that bis(2-ethylhexyl)phthalate alone induced high levels of testicular and epididymal abnormalities, which included atrophy and lack of development. Furthermore, several male rats from different litters displayed hemorrhagic testes. Gray *et al*. (1999) concluded that the testis is a direct target of bis(2-ethylhexyl)phthalate during perinatal life. Zacharewski *et al*. (1998) reported that the phthalates (e.g., di-n-butylphthalate, butylbenzyl phthalate, and dihexylphthalate) showed weak estrogenic activity in some *in vitro* assays at high concentrations.

In human studies, Gray *et al*. (1999) reported that bis(2-ethylhexyl)phthalate adversely affected the development of Sertoli cells, testicular cells that are central to sperm production. Sertoli cells damaged during development resulted in low sperm count in adulthood. Gray *et al*. (1999) also reported that bis(2-ethylhexyl)phthalate does not damage Sertoli cells directly, but that damage is caused by monoethylhexylphthalate, a bis(2-ethylhexyl)phthalate metabolite.

Toxic effects observed in rats and mice that have been reported from phthalate exposure experiments included hepatomegaly, increased numbers of hepatic peroxisomes, fetotoxicity, teratogenicity, and testicular damage. Alterations in liver have

been reported similar to those caused by metabolic stress (Jobling *et al*., 1995; Soto *et al*., 1995).

Sullivan e*t al*. (1993) reported a NOEC for bis(2-ethylhexyl)phthalate at 69 mg/kg of body weight per day in rat. Also, for rat testicular effects it was more recently proposed that the NOEC for bis(2-ethylhexyl)phthalate should be as low as 3.7 mg/kg of body weight per day (CSTEE, 1998).

Rhodes *et al*. (1995) conducted chronic toxicity tests on the waterflea (*Daphnia magna*, 14 phthalates) and on rainbow trout (*Oncorhynchus mykiss*, 6 phthalates). They reported that the toxicity for both species increased as the water solubility of the low molecular weight phthalates decreased. The maximum acceptable toxicant concentration of low molecular weight phthalates for *D. magna* ranged from 0.63 to 34.8 mg/L. For several high molecular weight phthalates, including bis(2-ethylhexyl)phthalate, the maximum acceptable toxicant concentration values ranged from 0.042 to 0.15 mg/L. Rhodes *et al*. (1995) also reported that for *D. magna* survival was equally or more sensitive than reproduction. The observed toxicity to *D. magna* from the high molecular weight phthalates was due to surface entrapment and not exposure to a dissolved aqueous-phase chemical (Rhodes *et al*., 1995). Rhodes *et al*. (1995) conducted early life-stage studies with rainbow trout and reported that dimethylphthalate affected survival and di-n-butylphthalate affected growth at 24 and 0.19 mg/L, respectively.

In other chronic toxicity experiments, Suggatt and Foote (1981) tested the green alga *Selenastrum* and reported an endpoint 96 h EC_{50} threshold concentration at 110 µg/L for butylbenzyl phthalate. In a flow-through study, Springborn Bionomics (1986) reported for mysid shrimp (*Mysidopsis bahia*) an endpoint 28-day LOEC of 170 µg/L for butylbenzyl phthalate effects on reproduction and growth. Also for butylbenzyl phthalate, LeBlanc (1984) reported a 30-day LOEC of 360 µg/L for fathead minnow (*Pimephales promelas*) based on egg hatching and larval survival and growth. For di-n-butylphthalate chronic toxicity tests using *Daphnia magna*, Kuhn *et al*. (1989) reported a 21-day NOEC of 500 µg/L based on parent survival.

In an acute toxicity experiment, Ozretich *et al*. (1983) reported a 96 h LC_{50} threshold concentration of 510 µg/L for shiner perch (*Cymastogaster aggregata*) exposed to butylbenzyl phthalate in a flow-through study. In a static bioassay experiment using invertebrate mysid shrimp (*Mysidopsis bahia*), Gledhill *et al*. (1980) reported a 96 h LC_{50} threshold concentration of 900 µg/L for butylbenzyl phthalate. In acute toxicity tests for di-n-butylphthalate, mysids showed a 96 h LC_{50} threshold concentration of 750 µg/L (EG&G Bionomics, 1984), and the midge (*Chironomus plumosus*) showed a 48 h EC_{50} threshold concentration of 760 µg/L (Streufert *et al*., 1980).

Occurrence

Water: The USGS study conducted on U.S. streams reported the occurrence of bis(2-ethylhexyl)phthalate (maximum concentration at 20 µg/L, median concentration at 7 µg/L) and bis(2-ethylhexyl)adipate (maximum concentration at 10 µg/L, median concentration at 3 µg/L) in water samples (Kolpin *et al*., 2002). In comparison, these concentrations were much higher than those found in this study: bis(2-

ethylhexyl)phthalate (maximum concentration at 7 ng/L) and bis(2-ethylhexyl)adipate (maximum concentration at 0.7 ng/L) (see Table 19).

Sediment: Vondracek *et al*. (2001) analyzed sediment samples collected from the Morava River and its tributaries (Czech Republic) for mutagenic, dioxin-like, and estrogenic activities. They reported that sediments were contaminated predominantly with polycyclic aromatic hydrocarbons and phthalates. The sum of the concentrations of phthalates in some sediment samples was reported to reach up to 3000 µg/kg dry weight of sediment.

Humans: Ingestion is identified as the principal pathway for di-n-butylphthalate exposure in humans, followed by lower exposures from indoor air and drinking water (IPCS, 1997). Di-n-butylphthalate is used as the principal plasticizer in the plastic wrapping material that is used to protect meat.

6. Triphenylphosphate

Regional Distributions

The distributions and concentrations of triphenylphosphate (TPP) in the regional samples are provided in Tables 2-8. Its chemical structure, common uses, and toxicity effects are provided in Table 14. TPP was found in Yerba Buena Island (maximum at 1 ng/L) and San Pablo Bay (0.01 ng/L) water samples (see Tables 3 and 6). TPP was also identified in the 1994 water blank samples (6 ng/L) and its concentration was greater than that found in the Yerba Buena Island water sample, which suggests that TPP in the water sample is likely due to contamination. TPP was not detected in the 1993 water sample blank, hence the TPP levels in the Yerba Buena Island and San Pablo Bay water samples are actual environmental concentrations. In comparison to the median concentration of TPP (40 ng/L) that was recently reported in the USGS study of streams (Kolpin *et al*., 2002), the maximum TPP concentration reported in this study (1 ng/L) was lower (Table 19).

Although the TPP concentrations were below the lowest LC_{50} value, it was not detected in San Francisco Estuary sediment samples, Sacramento and San Joaquin River water samples, or in POTW wastewater effluent samples. TPP was also not detected in any other sample blanks. The concentrations of TPP in the water samples did not exceed the lowest LC_{50} value for the most sensitive indicator aquatic species (98 µg/L, Table 2).

Triphenylphosphate should not be overlooked as an important component of environmental and human health concern. Its distribution and concentrations in present day San Francisco Estuary environmental samples and ecosystem impacts, if any, remain unknown. General information collected from the published literature on the characteristics, occurrence, toxicological effects and threshold levels of triphenylphosphate is included below.

Characteristics

Triphenylphosphate (TPP) belongs to the chemical class of organophosphates. TPP is a non-flammable, non-explosive, colorless, crystalline substance with an octanol/water partition coefficient (log K_{ow}) ranging from 4.61-4.76. TPP is a widely used flame retardant in video monitors and a plasticizer in some pesticides, gasoline additives, and synthetic motor oils (Ahrens *et al*., 1978). Its entry into the aquatic environment has been identified to occur primarily through urban runoff from hydraulic fluid leakage, leaching from vinyl plastics, and from manufacturing processes (Ahrens *et al*., 1978; Mayer *et al*., 1981; WHO, 1990). TPP is a component of flame-retardant hydraulic fluids and fluid additives used in commercial and military aircraft (David and Seiber, 1999). TPP is rapidly adsorbed to aquatic sediments due to its low water solubility (0.73-2.1 mg/L) and high soil adsorption potential.

Toxicology and Thresholds

A detailed review on the toxicology of TPP has been previously published (IPCS, 1991). Mayer *et al*. (1981) showed that the growth and survival of rainbow trout fry were not affected when they were exposed to 1.4 µg/L TPP. In separate studies conducted by Mayer *et al*. (1981) and Palawski *et al*. (1983), using 0.23 mg/L TPP, they reported significantly reduced survival rates for fathead minnow fry, and the growth of the survivors and their hatchability were not affected. Wagemann *et al*. (1974) and Lockhart *et al*. (1975) reported that sublethal effects of TPP on fish include morphological and behavioral abnormalities. Additionally, spinal curvature was observed in rainbow trout exposed to TPP for 24-72 h at concentrations near the LC_{50} (Sasaki *et al*., 1981; Palawski *et al*., 1983).

Ahrens *et al*. (1978) reported that goldfish death occurred in a 20-liter water tank in which a piece (18 x 38 cm) of car seat upholstery containing TPP (concentration not stated) had been immersed. The goldfish showed histopathological lesions in the small blood vessels of the gills, brain, spinal cord, pseudobranch, and kidneys. In a separate study, Palawski, *et al*. (1983) reported that the immobility of fish exposed to TPP at 0.21-0.29 mg/L disappeared within 7 days after exposure was halted.

The International Programme on Chemical Safety (IPCS, 1991) reports that TPP is acutely toxic to fish, shrimps, and daphnids. In experimental studies, the 96-h LC_{50} threshold concentrations for TPP to exposed fish ranged from 0.36 mg/L for rainbow trout (Palawski *et al*., 1983) to 290 mg/L for bluegill (Dawson *et al*., 1977). The oral LD_{50} threshold concentration has been estimated at >6.4 g/kg for rats and >2 g/kg for chickens (IPCS, 1991). TPP was not teratogenic in Sprague-Dawley rats at doses up to 690 mg/kg of body weight (IPCS, 1991).

Occurrence

Water: There are very few studies on the occurrence of TPP in natural water. Mayer *et al*. (1981) identified TPP in Mississippi River water samples at concentrations ranging from 100-7900 ng/L. Sheldon and Hites (1978) found TPP in Delaware River water samples ranging from 11-400 ng/L. Water samples collected from the Kanawa

River (USA) approximately 13 km downstream of an aryl phosphate manufacturing plant outfall showed TPP concentrations ranging from 300-1200 ng/L (Boethling and Cooper, 1985).

Drinking Water: Lebel *et al*. (1981) analyzed drinking water samples from 12 Eastern Ontario water treatment plants and found TPP levels ranging from 0.3-2.6 ng/L. TPP was also detected in 11 out of 12 samples of drinking water obtained from water treatment plants located around the Great Lakes at concentrations ranging from 0.2 to 4.8 ng/L (Williams *et al*., 1982). Sheldon and Hites (1979) reported a relatively high level of TPP (30 ng/L) in finished drinking water sampled from a water treatment plant located near a sewage treatment plant handling industrial effluents.

Sediment: Trialkyl and triaryl phosphates have been detected in water and sediments sampled near major industrialized sites (Konasewich *et al*., 1978; Sheldon and Hites, 1978, 1979; Mayer *et al*., 1981; Williams and Lebel, 1981; Aldous, 1982; Williams *et al*., 1982; Ishikawa *et al*., 1985). For example, Mayer *et al*. (1981) found TPP levels of 1000-4000 µg/kg in sediment from the Saginaw River sampled 1.6-3.2 km downstream from several automobile parts manufacturing plants. In addition, Mayer *et al*. (1981) also detected TPP at concentrations ranging from 10-200 µg/kg at Waukegan Harbor (Illinois), Upper Saginaw River (Michigan), the Mississippi River at St. Louis (Missouri), and the Kanawha River at Winfield (West Virginia). Kenmotsu *et al*. (1980) identified the adsorption coefficient of TPP on marine sediments as 59. Muir *et al*. (1982) showed that TPP was rapidly equilibrated (<10 h) with bottom sediment in a shallow pond.

Air: Carlsson *et al*. (2000a) identified triphenylphosphate in an indoor office environment. The emission sources were computer video display units with outer covers that were composed of up to 10% triphenylphosphate. The concentrations in air decreased from 100 ng/m^3 at day 1 of use to 10 ng/m^3 after 183 days. Yasuda (1980) reported TPP concentrations in air samples collected over rural and urban areas ranging from 0.5-1.4 ng/m^3 and 0.9-14.1 ng/m^3, respectively.

Aquatic Biota: Muir *et al*. (1983) treated six tissues of fish with radiolabeled ^{14}C-TPP. Liver tissue showed the highest concentration (10 µg/g at 4 h post-treatment) and also the highest rate of ^{14}C-TPP depuration. The rapid clearance from liver tissue was reported as due to TPP metabolism. The clearance rate constant for rainbow trout was higher than that for fathead minnows by 50% (Muir *et al*., 1983). Lombardo and Egry (1979) reported TPP levels of 60-150 µg/kg in carp and goldfish sampled at Waukegan Harbor near a site where aryl phosphate hydraulic fluids were commonly used. Mayer *et al*. (1981) detected concentrations of 100-600 µg/kg in 16 out of 82 samples collected in several rivers in the United States.

Wong and Chau (1984) reported that TPP was toxic to green algae. Algal growth was completely inhibited at concentrations of 1 mg/L or more but stimulated at lower levels of exposure (0.1 and 0.05 mg/L). Wong and Chau (1984) also showed that TPP at 0.1, 1.0, and 5.0 mg/L reduced the *Anabaena flos-aquae* nitrogenase activity to 84, 77, and 68% of the control value, respectively.

7. Pesticides

Regional Distributions

The distributions and concentrations of the pesticide compounds that were identified in the samples are provided in Tables 2-8. Their chemical structures, common uses, and toxic effects are provided in Table 15. The RMP routinely monitors for some pesticides in San Francisco Estuary water, sediment, and tissue samples. The concentrations and distributions of the routinely monitored pesticides can be found in the annual reports of the Regional Monitoring Program that are published by the San Francisco Estuary Institute.

Pesticides are intentionally released to the terrestrial environment through agricultural and household application or to the aquatic environment through direct application (e.g., aquatic herbicide treatment of water bodies such as irrigation canals, drinking water reservoirs, ditches, lakes and ponds). Some pesticides (e.g., legacy pollutants) have been shown to persist in the environment (e.g., organochlorines), induce toxicity (e.g., Endrin), bioaccumulate (e.g., Heptachlor), and cause cancer (e.g., Aldrin and Dieldrin). Pesticides are generally detected in water as pulses or spikes that correspond to their use and rainfall patterns. Their input into water bodies at concentrations that can induce acute and chronic toxicity on aquatic biota (plants and animals) depending on dosage and bioavailability can be detrimental to an aquatic ecosystem. Monitoring for pesticides (legacy and new) in the San Francisco Estuary is necessary to prevent such compounds from potentially harming the aquatic ecosystem.

Pesticides identified in the San Francisco Estuary samples that are not routinely monitored included the insecticide iridomyrmecin, and the herbicides propyzamide, benfluralin, and trifluralin (see Tables 2 and 15). Iridomyrmecin is a compound that was initially isolated from ants of the genus *Iridomyrmex*. It is generally used as an insecticide and bactericide and was found in a water sample from Dumbarton Bridge (Table 2). Propyzamide, benfluralin, and trifluralin are microtubule assembly inhibitors that are applied to soils for pre-emergent control of annual grasses and annual broad leaf weeds (British Crop Protection Council, 2000). These herbicides were only found in San Francisco Estuary water samples and can each induce toxicity to aquatic biota.

A herbicide that was identified only in a POTW wastewater sample was 2,6-dichlorobenzonitrile, also known as dichlobenil. This herbicide inhibits plant cell wall (cellulose) biosynthesis (British Crop Protection Council, 2000). It is used for selective weed control of annual and many perennial weeds in woody ornamentals, fruit orchards, vineyards, bush fruit, forest plantations, and public green areas. It is also used to control floating, emergent, and submerged aquatic plant growth in non-flowing water. It has been shown to induce toxicity in some aquatic species (various fish species: LC_{50} (96 h) 3.8-13 mg/L; Daphnia: LC_{50} (48 h) 6.2 mg/L; British Crop Protection Council, 2000).

It is important to mention that the concentrations of these pesticides in the samples examined did not exceed the lowest LC_{50} values for some of the most sensitive indicator aquatic species (Table 2). Because these pesticides can induce toxicity on aquatic biota it is recommended that future work in the San Francisco Estuary include

screening for these pesticides, among the others that are routinely screened in the RMP trace organics monitoring program.

8. Petroleum

Regional Distributions

Although careful measures are taken to prevent petroleum contamination in water bodies, small amounts of uncombusted lubricating oil and gasoline are often unavoidably introduced into water during outboard and inboard motor operation, repairs, fueling, and pumping of bilge from boat engine compartments. Petroleum products were identified as a major source of solvent-extractable organic chemicals in most of the San Francisco Estuary sediment samples (Appendices 25-28) and as a minor source in some of the water samples. The primary fossil fuel organic components identified in sediment and water samples include the n-alkanes, isoprenoids, tricyclic terpanes, hopanes, steranes, polycyclic aromatic hydrocarbons (PAH), and unresolved complex mixture (UCM). The San Francisco Estuary sediments represent a major environmental sink for oil, refined petroleum products, and their combustion alteration products. In the early years of the RMP, total petroleum hydrocarbon concentrations for sediments were reported, but this information was dropped in later years.

Petroleum hydrocarbon pollution and contamination in water bodies such as estuaries and lakes can be an obvious phenomenon (e.g., crude oil spill), whereas in low-level chronic cases it is not as clearly obvious. Petroleum contamination in the aquatic environment may originate from various sources, such as combustion engine emissions via atmospheric deposition and urban stormwater runoff, crude oil spills, and natural oil seepage. Boats and other watercraft, such as jet skis, introduce petroleum hydrocarbons to the water, which have unknown effects on the ecosystem. Outboard engines release their oil-enriched exhaust at and beneath the water surface. Particulate matter and volatile combustion products from inboard engine exhaust are injected into the water directly.

Petroleum is a complex mixture of organic compounds that includes low concentrations of polycyclic aromatic hydrocarbons (PAH) that impart the carcinogenic, genotoxic, and mutagenic properties to the total mixture (Cerniglia, 1984; Farrington, 1980; Farrington and Meyers, 1975; Heitcamp and Cerniglia, 1987). In addition, the volatile and more water-soluble petroleum components have been cited to cause detrimental effects on fish reproduction and behavior, and on water quality (Cranwell, 1975).

Petroleum was identified in GC-MS traces by its characteristic chemical signature which includes the homologous series of n-alkanes, an unresolved complex mixture (UCM), polycyclic aromatic hydrocarbons (PAH), and molecular biomarkers (extended tricyclic terpanes, hopanes, steranes, and diasteranes). Biomarkers are organic compounds of biological origin that have been geologically matured and retain their original structure or molecular configuration such that they can be used as tracers to identify fossil fuel sources.

The n-alkanes are derived from a variety of sources and their carbon number distributions are generally useful for differentiating between terrestrial and marine source materials (Philp and Mansuy, 1997). For example, vascular plants synthesize epicuticular waxes as odd carbon number n-alkane hydrocarbons usually in the C_{25}-C_{33} range, while marine plants synthesize short chain odd carbon number n-alkanes C_{15}-C_{19} (Peters and Moldowan, 1993). Thus, an environmental sample that shows a dominance of odd carbon number high molecular weight n-alkanes is indicative of a terrestrial source of this material. In crude oils, the high molecular weight n-alkanes inherited from terrestrial plants are normally diluted by hydrocarbons from kerogen degradation, which increases the even number n-alkane concentrations, resulting in a ratio of odd carbon number to even carbon number n-alkanes for petroleum of around 1.0 (Simoneit, 1978). Thus, such a distribution is typical in petroleum containing samples that do not have a major input of n-alkanes from terrestrial plant sources. In the Estuary sediment samples, n-alkanes were detected in the GC-MS data by the mass fragmentogram plot of the m/z 85 key ion (Fig. 7). The distribution generally shows n-alkanes ranging from C_{17} to C_{33}, with C_{29} as the most abundant n-alkane. This sample is petroleum contaminated as indicated by the presence of the isoprenoid hydrocarbons (pristane and phytane), unresolved complex mixture (UCM), and the molecular biomarkers (tricyclic terpanes, hopanes, diasteranes, and steranes). However, the n-alkane petroleum signature is dwarfed by the odd carbon number n-alkanes ($>C_{25}$) that are derived from the terrestrial input of plant waxes.

The isoprenoid hydrocarbons pristane and phytane have been used together as specific indicators for the presence of petroleum residues (Peters and Moldowan, 1993). They are mature biomarkers generally found in all crude oils and are stable in the environment. Pristane and phytane have specific chemical structures that are unique to their source, and together, they are not synthesized by contemporary biota. However, a high concentration of pristane alone can be derived from zooplankton. Pristane, but not phytane, is a major component found in marine zooplankton body fat and may be used for maintaining buoyancy in the water column (Blumer *et al*., 1963). These isoprenoids were identified in most of the sediment samples (Fig. 7).

The unresolved complex mixture (UCM), or broad “hump” that is associated with the heavier compounds in petroleum and lubricating oils, results from a mixture of branched and cyclic hydrocarbons, which generally indicates a petrogenic hydrocarbon input from heavier hydrocarbon fractions of petroleum (Brassel and Eglinton, 1980). The UCM is always present in unburned petroleum emissions; however, its chemical components cannot be fully determined by gas chromatography-mass spectrometry. Its major input vector into environmental systems is from engine lubricating oils. The UCM was identified in most of the sediment samples (Figures 5-7; Appendices 25-28) and its major pathway into the San Francisco Estuary is likely from urban runoff or crude oil spills.

Rowland *et al*. (2001) showed that the monoaromatic components that are present in the UCM from crude oil, elicited a sublethal toxic response in the marine mussel *Mytilus edulis*. Coastal United Kingdom mussels with unexplained impaired health were shown to contain substantial UCM burdens (range 271-3975 µg/g dry weight compared to controls at 9 µg/g dry weight collected from an unpolluted site). The monoaromatic compounds in the UCM were identified as alkylbenzenes and C-ring monoaromatic

steroids. Because the UCM is highly resistant to biodegradation, persistent, and widely distributed in San Francisco Estuary sediments, it is recommended that the UCM toxic effects on marine biota be studied in more detail.

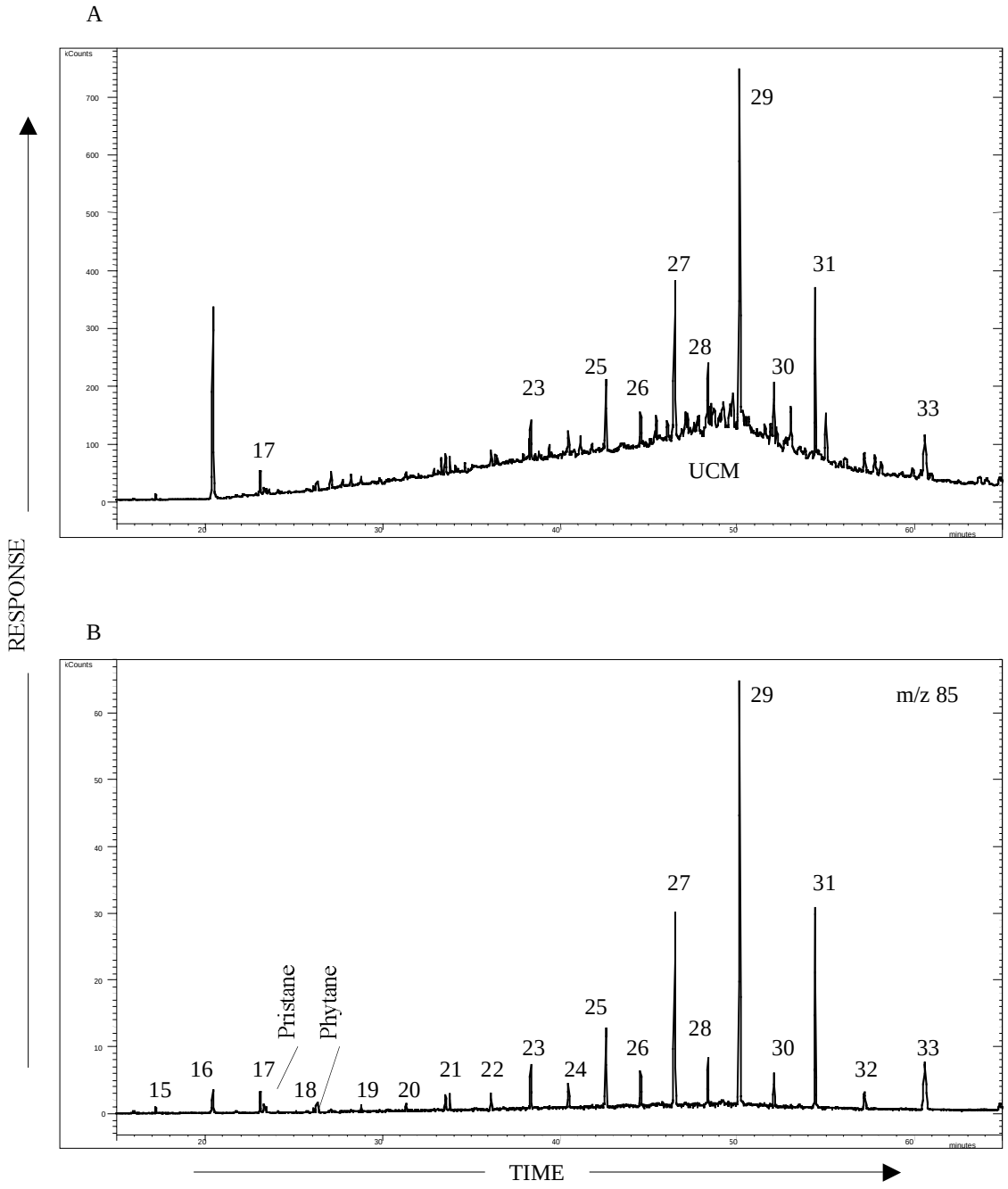

Figure 7. GC-MS traces of a 1993 sediment sample from Dumbarton Bridge showing petroleum aliphatics: A) total ion current trace of hydrocarbon fraction 1, and B) n-alkanes and the isoprenoids pristane and phytane (detected in data of A by the key fragment ion m/z 85). The n-alkane carbon numbers are indicated. Abbreviation: UCM = unresolved complex mixture.

The petroleum biomarkers are indicator compounds that can be used for determining the sources of organic matter in the environment (e.g., Simoneit 1978, 1986). As applied here, biomarkers characteristic of petroleum products are identified to confirm such an origin for extractable organic matter. The petroleum biomarkers are tricyclic terpanes, 17α(H)-hopanes, steranes and their rearranged analogs (diasteranes) that are minor but unique components in petroleum products such as lubricating oils (Beiger *et al*., 1996; Peters and Moldowan, 1993; Rogge *et al*., 1993). The extended tricyclic terpane and hopane biomarkers were detected in the 1993 sediment sample from Dumbarton Bridge by the mass fragmentogram plot of the m/z 191 key ion (Fig. 8, example chemical structures are indicated on the figure). The extended tricyclic terpanes ranged from C_{24} to C_{26} and were dominated by the C_{24} compound. The dominant hopanes, which contained the 17α(H),21β(H) configuration, were identified as 17α(H),21β(H)-30-norhopanes and 17α(H),21β(H)-hopanes with the diastereomeric 22-S and 22-R configurations. These hopanes were previously identified in San Francisco Estuary sediment samples as two of the most recalcitrant organic compounds from petrogenic sources (Hostettler *et al*., 1999). The 5α(H),14α (H),17α(H)-steranes (C_{27}-C_{29}) and the diasteranes (C_{27} and C_{28}) were also found in Dumbarton Bridge sediments as shown by the key ion plot of m/z 217 (Fig. 9). Steranes are derived from naturally occurring sterols. The ααα-steranes were previously identified as components of petroleum contaminated sediments in the San Francisco Estuary (Hostettler *et al*., 1999). The distribution of the ααα-steranes (C_{27}>C_{28}>C_{29}) suggests a marine autochthonous origin for the organic matter that contributed to this petroleum (terrestrial plants, C_{29}>C_{28}>C_{27}) (Peters and Moldowan, 1993). Polycyclic aromatic hydrocarbons (PAH) are also organic components in petroleum and they were identified in the environmental samples (Table 2). PAH will be discussed in detail in the next section.

9. Polycyclic Aromatic Hydrocarbons

Regional Distributions

Polycyclic aromatic hydrocarbons (PAH) are present at trace levels in petroleum and as major components in thermal combustion processes. The RMP routinely monitors PAH in San Francisco Estuary water, sediment, and tissue samples. PAH can originate from a variety of anthropogenic sources in urban areas by thermal combustion processes and vehicular emissions (e.g., petroleum, heating and cooking oils, etc.) and from biomass burning (e.g., wild fires, wood burning, controlled field burning) (Simoneit, 1984). Another source of PAH is high temperature combustion that emits the high molecular weight PAH (4 rings or more) as previously described for many urban areas (Neff, 1979). High molecular weight PAH (e.g., fluoranthene, pyrene, benzo[a]pyrene, etc.) were routinely identified in the San Francisco Estuary water and sediment samples. These compounds are especially obvious in GC-MS chromatograms of the F2 aromatic fractions from sediment samples (see Appendices 25-28).

Combustion emissions from vehicles using petroleum-derived fuels and lubricants contain PAH with a relatively high amount of alkyl substituents (Marcus *et al*., 1988). The typical indicators used are the phenanthrene/anthracene series, which are also

routinely reported by the RMP. This signature is distinguishable from the PAH emitted by biomass burning sources, where phenanthrene/anthracene (P/A) series would show an enriched content of C2 and C4 substituted PAH products. The presence of C2 and C4 substituted PAH products such as pimanthrene and retene, alteration products from burning of conifer resin compounds, in some of the San Francisco Estuary water samples indicates that biomass burning is also a source of PAH to the aquatic environment (Ramdahl, 1983; Standley and Simoneit, 1987, 1994) (Figure 2; Appendix 3). The C4 substituted PAH, retene, was found in Grizzly Bay water (1 ng/L). Retene has been previously proposed as a tracer for conifer combustion sources (Ramdahl, 1983). The amount of PAH that enters into the Estuary from biomass burning sources is currently unknown and expected to be much less than the contribution from vehicular combustion emissions due to the Estuary's urban location.

In general, the mixtures of PAH identified in the environmental samples cannot be attributed to a single source. However, both unburned and combusted fossil fuels (lubricating oil, crude oil, vehicular exhaust residues) do impart their signature in the sediments. PAH are major components of the total extractable organic matter present in sediments and are minor components in water.

10. Other Synthetic Compounds

Regional Distributions

The distributions and concentrations of other synthetic compounds that were identified in the regional samples are provided in Table 2. Their chemical structures, common uses, and summary of toxic effects are provided in Table 17. Some of these compounds were major components in samples as was apparent by their large peaks in the GC-MS chromatograms, while others were detected but only present as minor components in the samples.

Several of these compounds are common ingredients in industrial, household, and personal care product formulations: chloroxylenol, an antiseptic and germicide used in cleaning agents; chlorophene, a bactericide; benzophenone, a fixative agent used in soaps and cosmetics; octylmethoxy cinnamate, a UV blocking agent used in sunscreens; iminostilbene, a possible biological metabolite of carbamazepine, an analgesic and anticonvulsant prescription drug; triclosan, a common bacteriostat and preservative used in personal care products such as shampoos, deodorants, cosmetics, and toothpastes; and methyl-triclosan, a bacterial metabolite of triclosan (Lindstrom *et al*. 2002). Methyl-chloro-triclosan was also identified, however, in POTW wastewater effluent only and is possibly a by-product of the chlorination treatment process. Another compound identified was 2,4',5-trichloro-p-terphenyl which is a heat resisting component that is commonly used in industrial hydraulic fluids.

It is not known if any these compounds are presently impacting the health of the aquatic ecosystem. Since some of the compounds identified above are common ingredients in industrial, household, and personal care product formulations, it is possible that their major pathway of input to the San Francisco Estuary is through discharge of

POTW wastewater effluent. If this is the case, their concentrations are expected to be much higher in environmental sample collected near wastewater effluent discharge sites.

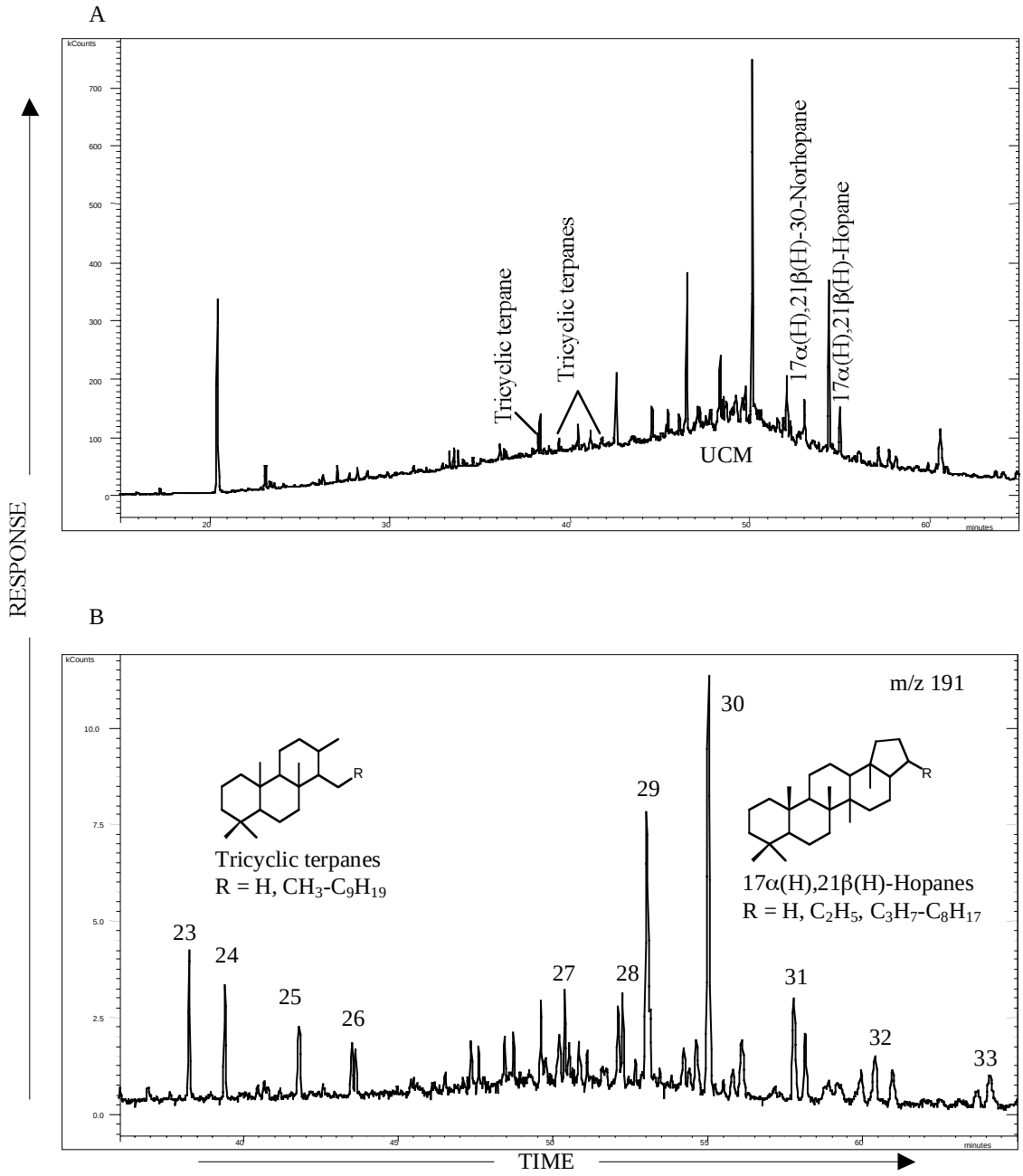

Figure 8. GC-MS traces of a 1993 sediment sample from Dumbarton Bridge showing petroleum terpanes and hopanes: A) total ion current trace of hydrocarbon fraction 1, and B) tricyclic terpanes and 17α(H),21β(H)-hopanes (detected in data of A by the key fragment ion m/z 191). Carbon numbers are indicated. Abbreviation: UCM = unresolved complex mixture.

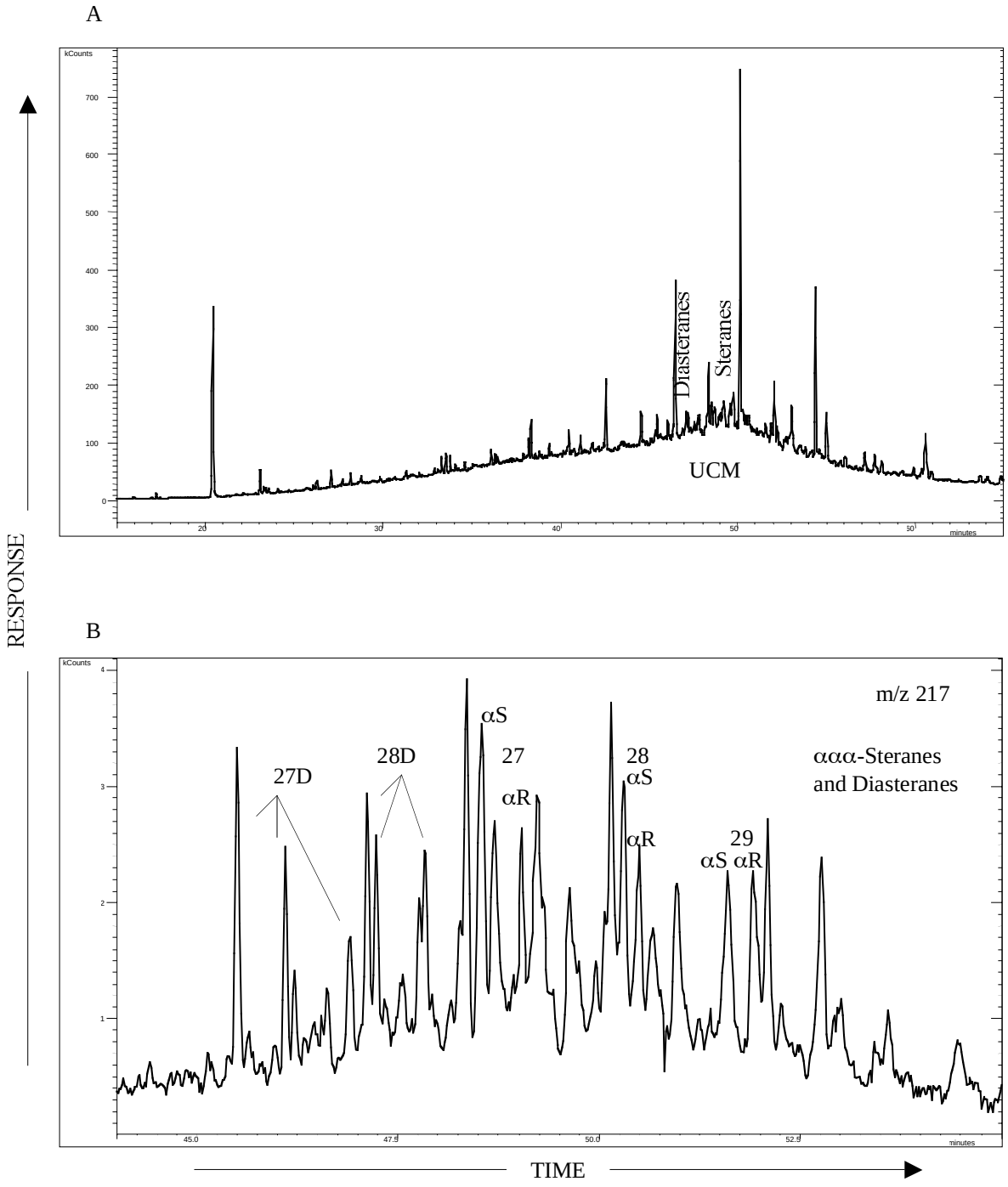

Figure 9. GC-MS traces of a 1993 sediment sample from Dumbarton Bridge showing petroleum steranes and diasteranes: A) total ion current trace of hydrocarbon fraction 1, and B) steranes and diasteranes (detected in data of A by the key fragment ion m/z 217). Carbon numbers are indicated. Abbreviations: D = diasterane, R and S indicate stereochemical configuration as determined from mass spectra, UCM = unresolved complex mixture.

IV. SUMMARY AND CONCLUSIONS

The archived GC-MS data were used to determine the concentrations and spatial distributions of trace organic compounds in the San Francisco Estuary environmental samples during the recent past. This information, when coupled with toxicological data, could be used to make preliminary assessments of the need to regulate their use in and around the San Francisco Estuary. Several individual compounds and compound groups identified in this study were recommended for screening in the 2002 RMP monitoring program because of their potential to persist in the environment, bioaccumulate in tissues, and induce toxicity depending on dosage and bioavailability (Appendix 32). These compounds were the polybrominated diphenyl ethers (PBDEs), phthalates, nitro and polycyclic musks, p-nonylphenol, and triphenylphosphate. The major sources of these compounds into the environment are the discharge of wastewater effluents, urban and agricultural runoff, soil erosion, and atmospheric deposition. The list of compounds that were recommended for screening in the 2002 RMP monitoring program is limited due to the high cost of conducting chemical analyses.

Although the concentrations reported for several of these compounds in water (1993, 1994) and sediment (1993) samples were below known toxicity thresholds (LC_{50}) and water quality criteria guidelines, there remains the possibility that their concentrations in present day San Francisco Estuary samples has increased. Therefore, the recommended compounds will be screened in water, sediment and tissue samples, except the nitro and polycyclic musk compounds which will be screened in tissue (bivalve) samples only. If a compound that was recommended for screening in the 2002 RMP monitoring program is not detected in the San Francisco Estuary samples or is found at concentrations that are far below toxicity thresholds, using the appropriate chemical methods that are designed for their analyses in a specific environmental medium (water, sediment, and tissue), then that compound will not be included for screening in the 2003 RMP monitoring program. Other compounds that were identified in this study, yet not recommended for screening (e.g., pesticides) in the 2002 RMP trace organics monitoring program, will be watched more closely in future special studies.

In the early 1990s during the time of sample collection and analysis, very little was known about the behavior, toxicity, bioaccumulation potential, transport, and fate of the recommended compounds once they entered the aquatic environment. It was suggested in early scientific studies and demonstrated in more recent studies that these compounds have the potential to adversely impact ecosystem and human health. Although the organic contaminant maximum concentrations that were observed were well below the reported LC_{50} value for some aquatic species, their present concentrations and adverse ecosystem effects (if any) in the San Francisco Estuary still remain unknown. The samples were collected at far-shore sampling locations along the spine of the Estuary. These organic contaminants are expected to reach concentrations that are much higher at near-shore sampling locations. It is also expected that they will be widely distributed in the San Francisco Estuary, Sacramento and San Joaquin River waters, sediments, and in fish and shellfish tissues.

It is important to mention that the most abundant organic constituents that are often identified in GC-MS chromatograms of environmental samples are not necessarily

the most important ones. For example, a compound present at a low level near the chromatographic baseline that has potential to bioaccumulate or induce a significant toxic effect at very low dose concentrations, can pose a greater threat to aquatic biota than a compound that is non-bioaccumulative, non-toxic, and present at a high level. Water and sediments are composed of heterogeneous organic mixtures and attempts to identify a single organic compound in the mixture that is responsible for an observed toxic effect to aquatic biota is very difficult and requires the use of sophisticated laboratory based toxicological tests.

Fossil fuels (i.e., crude oil and petroleum) were identified as the most dominant source of solvent-extractable organic matter in most of the Estuary sediment samples and as a minor component in some water samples. The polycyclic aromatic hydrocarbons (PAH) and the unresolved complex mixture (UCM) associated with petroleum can be harmful to aquatic biota. Our results show that the San Francisco Estuary sediments are an environmental sink for crude oil, refined petroleum products, and their combustion alteration derivatives.

Information collected from the scientific literature that addresses the environmental distributions, characteristics, occurrences, and toxicity of individual compounds and compound classes of concern that were identified in this study has been provided. Still, more definitive information and basic research on compound behavior (e.g., partitioning between environmental mediums and biological tissue), bioavailability (e.g., biochemical reactivity and toxicity) and fate (e.g., bioaccumulation, biodegradation, burial in sediments, etc.) in the San Francisco Estuary is needed in order to link these newly identified contaminants to any suspected adverse impacts.

V. ACKNOWLEDGEMENTS

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Table 1. Common natural compound groups identified in samples.

Compound Group	Plant Source	Examples	Product
I. Homologous series			
n-Alkanes	epicuticular waxes	heptacosane (C_{27}), nonacosane (C_{29})	natural
n-Alkenes	epicuticular waxes	heptacosene ($C_{27:1}$), nonacosene ($C_{29:1}$)	altered
n-Alkanals	epicuticular waxes	hexacosanal (C_{26}), octacosanal (C_{28})	natural
n-Alkanoic acids	internal lipid substances	docosanoic acid (C_{22}), tetracosanoic acid (C_{24})	natural
n-Alkanols	epicuticular waxes	hexacosanol (C_{26}), octacosanol (C_{28})	natural
n-Alkanones	epicuticular waxes	pentacosanone (C_{25}), heptacosanone (C_{27})	natural
II. Biomarkers			
Monoterpenoids (C_{10})	essential oils	calamanene, thujone	natural
Sesquiterpenoids (C_{15})	essential oils	isocedrol, patchouli alcohol	natural
Diterpenoids (C_{20})	gymnosperm resin, wax	abietic acid, dehydroabietic acid, retene	natural/altered
Steroids	internal lipid substances	stigmast-3-ene, stigmasta-3,5-diene	altered
III. Other			
Isoprenoids	internal lipid components	phytol, squalene	natural
Wax esters	epicuticular waxes	dodecyl dodecanoate, pentadecyl dodecanoate	natural

Table 2. Common synthetic compounds identified in samples.

Compound Group	MW	Formula	CAS#	Use	Max (ng/L)	LC_{50}	Location	Medium	Year
I. Alkylbenzenes									
1-Ethyl-octylbenzene	218	$C_{16}H_{26}$	4621-36-7	surfactant	0.4	-/0	Sacramento River	water	1994
1-Methyl-nonylbenzene	218	$C_{16}H_{26}$	4537-13-7	surfactant	1	-/0	Sacramento River	water	1994
1-Butyl-heptylbenzene	232	$C_{17}H_{28}$	NA	surfactant	1	-/0	Sacramento River	water	1994
1-Ethyl-nonylbenzene	232	$C_{17}H_{28}$	4536-87-2	surfactant	1	-/0	Sacramento River	water	1994
1-Methyl-decylbenzene	232	$C_{17}H_{28}$	4536-88-3	surfactant	2	-/0	Sacramento River	water	1994
Undecylbenzene	232	$C_{17}H_{28}$	6742-54-7	surfactant	1	-/0	Sacramento River	water	1994
1-Ethyl-decylbenzene	246	$C_{18}H_{30}$	2400-00-2	surfactant	1	-/0	Sacramento River	water	1994
1-Methyl-undecylbenzene	246	$C_{18}H_{30}$	2719-61-1	surfactant	2	-/0	Sacramento River	water	1994
1-Ethyl-undecylbenzene	260	$C_{19}H_{32}$	4534-52-5	surfactant	0.2	-/0	Sacramento River	water	1994
1-Methyl-dodecylbenzene	260	$C_{19}H_{32}$	4534-53-6	surfactant	1	-/0	Sacramento River	water	1994
II. Nitro and Polycyclic Musks									
Phantolide	244	$C_{17}H_{24}O$	15323-35-0	fragrance	4	-/0	Grizzly Bay	water	1994
Galaxolide	258	$C_{18}H_{26}O$	1222-05-5	fragrance	227	-/0	Dumbarton Bridge	water	1994
Tonalide	258	$C_{18}H_{26}O$	88-29-9	fragrance	3	-/0	Sacramento River	water	1993
Traseolide	258	$C_{18}H_{26}O$	68140-48-7	fragrance	14	-/0	POTW only	effluent	1998
4-Amino-musk xylene	267	$C_{12}H_{17}N_3O_4$	107342-55-2	fragrance	1	-/0	Dumbarton Bridge	water	1993
Musk ambrette	268	$C_{12}H_{16}N_2O_5$	83-66-9	fragrance	5	-/0	Yerba Buena Is.	water	1993
Musk ketone	294	$C_{14}H_{18}N_2O_5$	81-14-1	fragrance	12	-/0	San Pablo Bay	water	1994
Musk xylene	297	$C_{12}H_{15}N_3O_6$	81-15-2	fragrance	0.2	-/0	San Pablo Bay	water	1993
III. Pesticides									
Iridomyrmecin	168	$C_{10}H_{16}O_2$	485-43-8	insecticide	3	-/0	Dumbarton Bridge	water	1994
2,6-Dichlorobenzonitrile	171	$C_7H_3Cl_2N$	1194-65-6	herbicide	5	3830/17[a]	POTW only	effluent	1998
Propyzamide	255	$C_{12}H_{11}Cl_2NO$	23950-58-5	herbicide	5	4700/1[a]	Sacramento River	water	1994
Benfluralin	335	$C_{13}H_{16}F_3N_3O_4$	1861-40-1	herbicide	0.1	200/6[a]	Dumbarton Bridge	water	1993
Trifluralin	335	$C_{13}H_{16}F_3N_3O_4$	1582-09-8	herbicide	1	7.2/79[a]	Grizzly Bay	water	1994
IV. Polybrominated Diphenyl Ethers									
Dibromo diphenyl ether	326	$C_{12}H_{10}Br_2O$	NA	flame retardant	0.1	-/0	POTW only	water	1998
Tetrabromo diphenyl ether	486	$C_{12}H_6Br_4O$	NA	flame retardant	5	-/0	Sacramento River	water	1994
Pentabromo diphenyl ether	565	$C_{12}H_5Br_5O$	NA	flame retardant	14	-/0	San Joaquin River	water	1994
Hexabromo diphenyl ether	644	$C_{12}H_4Br_6O$	NA	flame retardant	2	-/0	San Joaquin River	water	1994

Table 2 (Cont'd). Common synthetic compounds identified in samples.

Compound Group	MW	Formula	CAS#	Use	Max (ng/L)	LC_{50}	Location	Medium	Year
V. Phenols and Related Compounds									
4-Methylene-2,6-di-tert-butyl-2,5-cyclohexadien-1-one	218	$C_{15}H_{22}O$	NA	BHT alteration product	58	-/0	San Pablo Bay	water	1994
Butylated hydroxy toluene	220	$C_{15}H_{24}O$	128-37-0	antioxidant	2502	1440/1[a]	Sacramento River	water	1994
2,6-Di-tert-butyl-1,4-benzoquinone	220	$C_{14}H_{20}O_2$	719-22-2	BHT alteration product	1	-/0	Dumbarton Bridge	water	1993
2,6-Di-tert-butyl-4-hydroxy-4-methyl-2,5-cyclohexadien-1-one	236	$C_{15}H_{24}O_2$	NA	BHT alteration product	78	-/0	Yerba Buena Is.	water	1993
3,5-Di-tert-butyl-4-hydroxy anisole	236	$C_{15}H_{24}O_2$	489-01-0	antioxidant	1	870/1[a]	POTW only	effluent	1998
2,6-Di-tert-butyl-1-methoxy-4-ethyl-benzene	248	$C_{17}H_{28}O$	NA	BHT alteration product	0.02	-/0	San Pablo Bay	water	1993
2,6-Di-tert-butyl-4-(methoxymethyl)-phenol	250	$C_{16}H_{26}O_2$	87-97-8	BHT alteration product	4	-/0	Sacramento River	water	1994
2,6-Di-tert-butyl-4-nitro-phenol	251	$C_{14}H_{21}NO_3$	728-40-5	BHT alteration product	4	-/0	San Joaquin River	water	1993
2,6-Di-tert-butyl-4-cyclohexyl-phenol	288	$C_{20}H_{32}O$	NA	BHT reaction product	2	-/0	Grizzly Bay	water	1993
2,6-Di-tert-butyl-4-(2,3-dimethyl-but-2-enyl)-phenol	288	$C_{20}H_{32}O$	NA	BHT reaction product	0.2	-/0	San Pablo Bay	water	1993
2,6-Di-tert-butyl-4-(2,3-dimethyl-3-hydroxy-butyl)-phenol	306	$C_{20}H_{34}O_2$	NA	BHT reaction product	2	-/0	Sacramento River	water	1994
2,6-Di-tert-butyl-4-(1-methyl-1-phenylethyl)-phenol	324	$C_{23}H_{32}O$	34624-81-2	antioxidant	98	-/0	Dumbarton Bridge	water	1994
2,4-Bis(1-methyl-1-phenylethyl)-phenol	330	$C_{24}H_{26}O$	2772-45-4	metabolite	14	-/0	Yerba Buena Is.	water	1994
2,4-Bis(1-methyl-1-phenylethyl)-6-tert-butyl-phenol	386	$C_{28}H_{34}O$	NA	metabolite	35	-/0	Sacramento River	water	1993
2,4,6-Tris(1-methyl-1-phenylethyl)-phenol	448	$C_{33}H_{36}O$	30748-85-7	antioxidant	4	-/0	San Joaquin River	water	1993
VI. Phthalates									
Di-n-butyl phthalate[d]	278	$C_{16}H_{22}O_4$	84-74-2	plasticizer	1096	300/36[b]	Dumbarton Bridge	water	1994
Butylbenzyl phthalate[d]	312	$C_{19}H_{20}O_4$	85-68-7	plasticizer	12	780/41[b]	Dumbarton Bridge	water	1994
Bis(2-ethylhexyl)adipate	370	$C_{22}H_{42}O_4$	103-23-1	plasticizer	1	480/3[c]	Yerba Buena Is.	water	1993
Bis(2-ethylhexyl)phthalate[d]	390	$C_{24}H_{38}O_4$	117-81-7	plasticizer	7	160/52[b]	Dumbarton Bridge	water	1994

Table 2 (Cont'd). Common synthetic compounds identified in samples.

Compound Group	MW	Formula	CAS#	Use	Max (ng/L)	LC_{50}	Location	Medium	Year
VII. Others									
Chloroxylenol	156	C_8H_9ClO	88-04-0	antiseptic	2	-/0	POTW only	effluent	1993
Benzophenone	182	$C_{13}H_{10}O$	119-61-9	fixative	0.4	9640/18[b]	Dumbarton Bridge	water	1993
Imonostilbene	193	$C_{14}H_{11}N$	256-96-2	from carbamazepine	6	-/0	POTW only	effluent	1998
Chlorophene	218	$C_{13}H_{11}ClO$	120-32-1	bactericide	12	-/0	POTW only	effluent	1998
p-Nonylphenol	220	$C_{15}H_{24}O$	25154-52-3	surfactant	19	98/22[b]	Sacramento River	water	1994
Retene	234	$C_{18}H_{18}$	483-65-8	biomass burning product	1	-/0	Grizzly Bay	water	1994
Octylmethyoxy cinnamate	290	$C_{18}H_{26}O_3$	5466-77-3	sunscreening agent	0.3	-/0	Grizzly Bay	water	1993
Triclosan (methyl)	302	$C_{13}H_9Cl_3O_2$	4640-01-1	triclosan metabolite	0.1	-/0	Dumbarton Bridge	water	1993
Triphenylphosphate	326	$C_{18}H_{15}O_4P$	115-86-6	flame retardant	1	280/13[a]	Yerba Buena Is.	water	1993
2,4',5-Trichloro-p-terphenyl	332	$C_{18}H_{11}Cl_3$	61576-93-0	industrial hydraulic fluids	0.5	-/0	San Pablo Bay	water	1993
Triclosan (methyl-chloro)	336	$C_{13}H_8Cl_4O_2$	NA	triclosan metabolite	0.2	-/0	POTW only	effluent	1998

Abbreviations: CAS# = Chemical Abstracts Service Registry Number, MW = chemical molecular weight, NA = not available, POTW = publicly owned treatment works.
*Lowest LC_{50} for most sensitive indicator species (µg/L)/no. of aquatic studies identified.
LC_{50} data from: U.S. EPA Ecotoxicology database. http://www.epa.gov/medecotx/quicksearch.htm (accessed March 2002).
[a]Rainbow trout (*Oncorhynchus mykiss*) - 96 h exposure LC_{50}; [b]Fathead minnow (*Pimephales promelas*) - 96 h exposure LC_{50};
[c]Water flea (*Daphnia magna*) - 48 h exposure LC_{50}; [d]Compound routinely detected in field blanks.

Table 3. Concentrations and distributions of select synthetic compounds in 1993 water samples.

Compound Group	Dumbarton Bridge (BA30) (D)	(P)	(D+P)	Yerba Buena (BC10) (D)	(P)	(D+P)	San Pablo Bay (BD20) (D)	(P)	(D+P)	Grizzly Bay (BF20) (D)	(P)	(D+P)	Blank (D+P)
I. Nitro and Polycyclic Musks													
Galaxolide	3	0.1	3	21	nd	21	0.3	0.04	0.3	0.3	0.1	0.4	0.04
Musk ketone	0.4	nd	0.4	nd	nd	nd	0.01	nd	0.01	0.01	nd	0.01	nd
II. Phthalates													
Bis(2-ethylhexyl)phthalate	0.1	0.4	0.5	0.2	1	1	0.5	0.4	1	0.5	0.1	1	0.5
Butylbenzyl phthalate	0.1	0.4	0.5	0.4	1	1	0.1	0.4	0.5	0.1	0.3	0.3	0.5
Di-n-butyl phthalate	6	0.1	6	7	0.4	7	0.7	1	1	0.4	1	1	4
III. Polybrominated Diphenyl Ethers													
Tetrabromo diphenyl ether	0.003	nd	0.003	nd	nd	nd	0.01	nd	0.01	nd	nd	nd	nd
Pentabromo diphenyl ether	nd	nd	nd	nd	nd	nd	0.02	nd	0.02	nd	nd	nd	nd
Hexabromo diphenyl ether	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
IV. Other													
Butylated hydroxy toluene	19	nd	19	nd	nd	nd	0.5	1	1	104	nd	104	0.1
p-Nonylphenol	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Trifluralin	0.1	nd	0.1	nd	0.01	0.01	1.1	nd	1	770	nd	770	nd
Triphenylphosphate	nd	nd	nd	1	nd	1	0.01	nd	0.01	nd	nd	nd	nd

Concentrations are in ng/L.
Abbreviations: nd is not detected, d is detected, D is dissolved organic fraction, P is particulate organic fraction.

Table 4. Concentrations and distributions of select synthetic compounds in 1993 river water samples.

	Sacramento River (Rio Vista)			San Joaquin River (Manteca)			Blank
Compound Group	(D)	(P)	(D+P)	(D)	(P)	(D+P)	(D+P)
I. Nitro and Polycyclic Musks							
Galaxolide	nd	0.4	0.4	nd	1	1	0.04
Musk ketone	nd	nd	nd	nd	nd	nd	nd
II. Phthalates							
Bis(2-ethylhexyl)phthalate	0.001	nd	0.001	nd	0.1	0.1	0.5
Butylbenzyl phthalate	0.002	nd	0.002	0.1	nd	0.1	0.5
Di-n-butylphthalate	0.008	24	24	0.2	54	54	4
III. Polybrominated Diphenyl Ethers							
Tetrabromo diphenyl ether	nd	nd	nd	nd	nd	nd	nd
Pentabromo diphenyl ether	nd	nd	nd	nd	nd	nd	nd
Hexabromo diphenyl ether	nd	nd	nd	nd	nd	nd	nd
IV. Other							
Butylated hydroxy toluene	15	nd	15	744	0.2	744	0.1
p-Nonylphenol	nd	nd	nd	nd	nd	nd	nd
Trifluralin	nd	nd	nd	nd	0.1	0.1	nd
Triphenylphosphate	nd	nd	nd	nd	nd	nd	nd

Concentrations are in ng/L.
Abbreviations: nd is not detected, d is detected, D is dissolved organic fraction, P is particulate organic fraction.

Table 5. Concentrations and distributions of select synthetic compounds in 1993 sediment samples.

Compound Group	Dumbarton Bridge (BA30)	Yerba Buena (BC10)	San Pablo Bay (BD20)	Grizzly Bay (BF20)	Blank
I. Nitro and Polycyclic Musks					
Galaxolide	nd	nd	nd	nd	nd
Musk ketone	nd	nd	nd	nd	nd
II. Phthalates					
Bis(2-ethylhexyl)phthalate	2	6	nd	7	1
Butylbenzyl phthalate	3	5	1	5	1
Di-n-butylphthalate	8	6	4	141	1
III. Polybrominated Diphenyl Ethers					
Tetrabromo diphenyl ether	nd	nd	nd	nd	nd
Pentabromo diphenyl ether	nd	nd	nd	nd	nd
Hexabromo diphenyl ether	nd	nd	nd	nd	nd
IV. Other					
Butylated hydroxy toluene	nd	nd	nd	nd	nd
p-Nonylphenol	nd	nd	nd	nd	nd
Trifluralin	nd	nd	nd	nd	nd
Triphenylphosphate	nd	nd	nd	nd	nd

Concentrations are in ng/g dry weight.
Abbreviations: nd is not detected, d is detected.

Table 6. Concentrations and distributions of select synthetic compounds in 1994 water samples.

	Dumbarton Bridge (BA30)			Yerba Buena (BC10)			San Pablo Bay (BD20)			Grizzly Bay (BF20)			Blank
Compound Group	(D)	(P)	(D+P)	(D)	(P)	(D+P)	(D)	(P)	(D+P)	(D)	(P)	(D+P)	(D+P)
I. Nitro and Polycyclic Musks													
Galaxolide	200	27	227	7	1	8	218	5	223	44	1	45	nd
Musk ketone	nd	nd	nd	0.3	nd	0.3	12	nd	12	1	nd	1	nd
II. Phthalates													
Bis(2-ethylhexyl)phthalate	4	3	7	1	1	2	1	0.1	1	0.03	0.2	0.3	27
Butylbenzyl phthalate	12	0.1	12	0.4	1	1	1	0.1	2	0.03	0.1	0.2	20
Di-n-butyl phthalate	172	924	1,096	0.4	24	24	276	61	337	20	4	24	14
III. Polybrominated Diphenyl Ethers													
Tetrabromo diphenyl ether	nd	nd	nd	nd	0.03	0.03	nd	nd	nd	nd	nd	nd	0.1
Pentabromo diphenyl ether	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.2
Hexabromo diphenyl ether	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
IV. Other													
Butylated hydroxy toluene	0.2	nd	0.2	1	nd	1	nd	nd	nd	6	nd	6	16
p-Nonylphenol	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Trifluralin	nd	nd	nd	nd	nd	nd	0.3	nd	0.3	1	0.02	1	nd
Triphenylphosphate	nd	nd	nd	0.4	0.1	1	nd	nd	nd	nd	nd	nd	6

Concentrations are in ng/L.
Abbreviations: nd is not detected, d is detected, D is dissolved organic fraction, P is particulate organic fraction.

Table 7. Concentrations and distributions of select synthetic compounds in 1994 river water samples.

Compound Group	Sacramento River (Rio Vista) (D)	(P)	(D+P)	San Joaquin River (Manteca) (D)	(P)	(D+P)	Blank (D+P)
I. Nitro and Polycyclic Musks							
Galaxolide	nd	0.1	0.1	1	nd	1	nd
Musk ketone	nd	nd	nd	nd	nd	nd	nd
II. Phthalates							
Bis(2-ethylhexyl)phthalate	0.1	0.02	0.1	0.03	0.02	0.1	27
Butylbenzyl phthalate	0.1	0.1	0.2	0.1	0.1	0.2	20
Di-n-butyl phthalate	1	5	5	7	0.1	7	14
III. Polybrominated Diphenyl Ethers							
Tetrabromo diphenyl ether	5	0.1	5	4	0.1	4	0.1
Pentabromo diphenyl ether	9	nd	9	14	nd	14	0.2
Hexabromo diphenyl ether	2	nd	2	2	nd	2	nd
IV. Other							
Butylated hydroxy toluene	2,502	nd	2,502	875	nd	875	16
p-Nonylphenol	19	nd	19	5	nd	5	nd
Trifluralin	0.2	nd	0.2	nd	0.1	0.1	nd
Triphenylphosphate	nd	nd	nd	nd	nd	nd	6

Concentrations are in ng/L.
Abbreviations: nd is not detected, d is detected, D is dissolved organic fraction, P is particulate organic fraction.

Table 8. Concentrations and distributions of select synthetic compounds in a 1998 wastewater final effluent sample.

Compound Group	Dissolved (D)	Particulate (P)	Total (D+P)	Blank (D only)
I. Nitro and Polycyclic Musks				
Galaxolide	162	15	177	0.2
Musk ketone	4	0.3	4	nd
II. Pesticides				
Chlorpyrifos	1	nd	1	nd
Diazinon	15	nd	15	nd
Oxadiazon	1	nd	1	nd
Trifluralin	nd	nd	nd	nd
III. Phthalates				
Bis(2-ethylhexyl)phthalate	2	0.02	2	1
Butylbenzyl phthalate	4	6	10	6
Di-n-butylphthalate	0.1	1	1	0.2
IV. Polybrominated Diphenyl Ethers				
Dibromo diphenyl ether	0.1	nd	0.1	nd
Tribromo diphenyl ether	nd	nd	nd	nd
Tetrabromo diphenyl ether	0.1	0.1	0.2	nd
Pentabromo diphenyl ether	nd	0.03	0.03	nd
Hexabromo diphenyl ether	nd	nd	nd	nd
V. Other				
Butylated hydroxy toluene	248	354	602	568
p-Nonylphenol	42	nd	42	0.03
Triphenylphosphate	nd	nd	nd	nd

Concentrations are in ng/L.
Abbreviations: nd is not detected, d is detected, D = dissolved organic fraction, P = particulate organic fraction.

Table 9. Nitro and polycyclic musks: chemical structures, common uses, and toxicity.

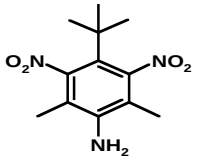
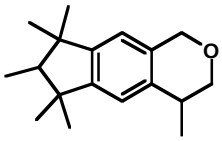
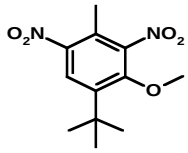
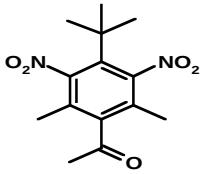
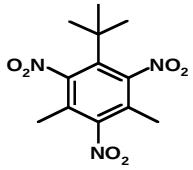
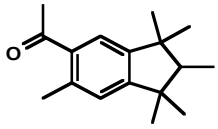
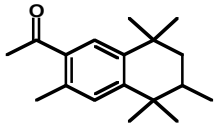
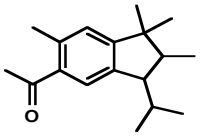
Compound Name	Chemical Structure	Common Uses	Toxicity
4-Amino-musk xylene CAS#: 107342-55-2 Formula: $C_{12}H_{17}N_3O_4$ MW: 267		Metabolite of musk xylene	Genotoxic; biodegradation product; bioaccumulates in aquatic species and humans
Galaxolide™ CAS#: 1222-05-5 Formula: $C_{18}H_{26}O$ MW: 258		Fragrances and personal care products	Bioaccumulates in aquatic species and humans
Musk ambrette CAS#: 83-66-9 Formula: $C_{12}H_{16}N_2O_5$ MW: 268		Fragrances and personal care products. Banned in the European Union	Neurotoxic; bioaccumulates in aquatic species and humans
Musk ketone CAS#: 81-14-1 Formula: $C_{14}H_{18}N_2O_5$ MW: 294		Fragrances and personal care products	Induces detoxifying liver enzymes; bioaccumulates in aquatic species and humans
Musk xylene CAS#: 81-15-2 Formula: $C_{12}H_{15}N_3O_6$ MW: 297		Fragrances and personal care products	Induces detoxifying liver enzymes and is genotoxic; bioaccumulates in aquatic species and humans
Phantolide™ CAS#: 15323-35-0 Formula: $C_{17}H_{24}O$ MW: 244		Fragrances and personal care products	Bioaccumulates in aquatic species and humans
Tonalide™ CAS#: 1506-02-1 Formula: $C_{18}H_{26}O$ MW: 258		Fragrances and personal care products	Bioaccumulates in aquatic species and humans
Traseolide™ CAS#: 68140-48-7 Formula: $C_{18}H_{26}O$ MW: 258		Fragrances and personal care products	Bioaccumulates in aquatic species and humans

Table 10. p-Nonylphenol: chemical structure, common uses, and toxicity.

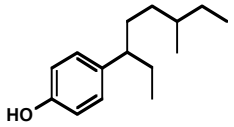
Compound Name	Chemical Structure	Common Uses	Toxicity
p-Nonylphenol CAS#: 25154-52-33 Formula: $C_{15}H_{24}O$ MW: 220		Preparation of lubricating oil additives, resins, plasticizers, pesticides, anionic detergents, surface-active agents, and toiletries; breakdown product of alkylphenol ethoxylates that are used as nonionic surfactants	Moderate potential for bioaccumulation in aquatic organisms; potential endocrine system disruptor

Table 11. Phenols and related compounds: chemical structures, common uses, and toxicity.

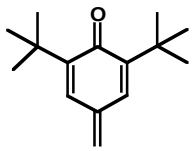
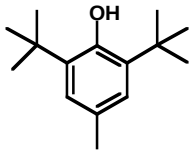
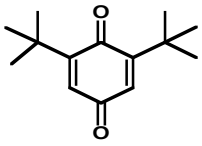
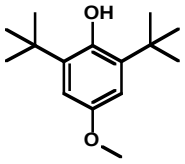
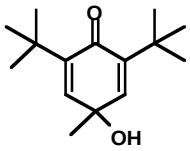
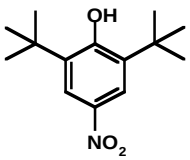
Compound Name	Chemical Structure	Common Uses	Toxicity
4-Methylene-2,6-di-tert-butyl-2,5-cyclohexadienenone CAS#: Not available Formula: $C_{15}H_{22}O$ MW: 218		Alteration (oxidation) product of butylated hydroxytoluene (BHT)	Unknown
Butylated hydroxy toluene CAS#: 128-37-0 Formula: $C_{15}H_{24}O$ MW: 220		Antioxidant for food, animal feed, petroleum products, synthetic rubbers, plastics, animal and vegetable oils, and soaps; anti-skinning agent in paints and inks	Unknown
2,6-Di-tert-butyl-1,4-benzoquinone CAS#: 719-22-2 Formula: $C_{14}H_{20}O_2$ MW: 220		Alteration (oxidation) product of butylated hydroxytoluene (BHT)	Unknown
3,5-Di-tert-butyl-4-hydroxy anisole CAS#: 489-01-0 Formula: $C_{15}H_{24}O_2$ MW: 236		Antioxidant and preservative especially in food, cosmetics, and pharmaceuticals; also in rubber and petroleum products	Suspected carcinogen
2,6-Di-tert-butyl-4-hydroxy-4-methyl-2,5-cyclohexadien-1-one CAS#: Not available Formula:$C_{15}H_{24}O_2$ MW: 236		Alteration (oxidation) product of butylated hydroxytoluene (BHT)	Unknown
2,6-Di-tert-butyl-4-nitro-phenol CAS#: 728-40-5 Formula: $C_{14}H_{21}NO_3$ MW: 251		Product of BHT reaction with nitrogen oxides in air	Unknown

Table 11 (Cont'd.). Phenols and related compounds: chemical structures, common uses, and toxicity.

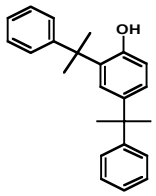
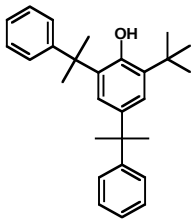
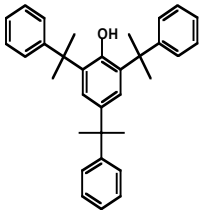
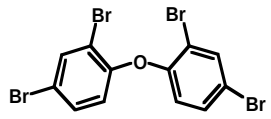
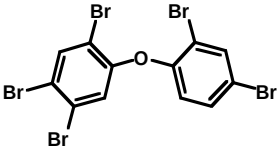
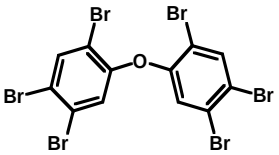
Compound Name	Chemical Structure	Common Uses	Toxicity
2,4-Bis(dimethyl)benzyl-phenol CAS#: 2772-45-4 Formula: $C_{24}H_{26}O$ MW: 330		Antioxidant and preservative or by-product of synthesis of related compounds	Unknown
2,4-Bis(dimethyl)benzyl-6-tert-butyl-phenol CAS#: Not available Formula: $C_{28}H_{34}O$ MW: 386		Antioxidant and preservative or by-product of synthesis of related compounds	Unknown
2,4,6-Tris(1-methyl-1-phenylethyl)-phenol CAS#: 30748-85-7 Formula: $C_{33}H_{36}O$ MW: 448		Antioxidant and preservative or by-product of synthesis of related compounds	Unknown

Table 12. Polybrominated diphenyl ethers: chemical structures, common uses, and toxicity.

Compound Name	Chemical Structure[a]	Common Uses	Toxicity
Tetrabromo diphenyl ether CAS#: NA Formula: $C_{12}H_6Br_4O$ MW: 486		Flame retardant in plastic products, polymers, resins and components of electronic devices, building materials and textiles	Accumulates and magnifies in biological tissues; potential endocrine system disruptor
Pentabromo diphenyl ether CAS#: NA Formula: $C_{12}H_5Br_5O$ MW: 565		Flame retardant in plastic products, polymers, resins and components of electronic devices, building materials and textiles	Accumulates and magnifies in biological tissues; potential endocrine system disruptor
Hexabromo diphenyl ether CAS#: NA Formula: $C_{12}H_4Br_6O$ MW: 644		Flame retardant in plastic products, polymers, resins and components of electronic devices, building materials and textiles	Accumulates and magnifies in biological tissues; potential endocrine system disruptor

[a]Structures shown are typical representations of polybrominated diphenyl ether (PBDE) compounds for which there are 209 possible congeners; NA = not available.

Table 13. Phthalates: chemical structures, common uses, and toxicity.

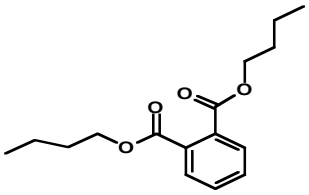
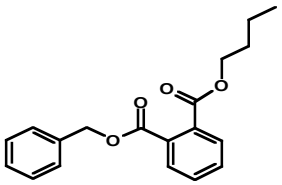
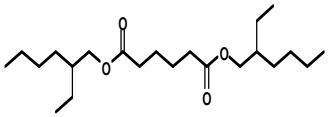
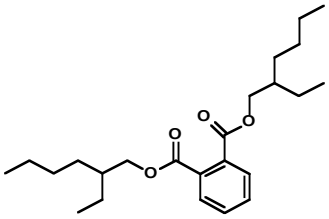
Compound Name	Chemical Structure	Common Uses	Toxicity
Di-n-butylphthalate CAS#: 84-74-2 Formula: $C_{16}H_{22}O_4$ MW: 278		Plasticizer added to polyvinyl chloride to increase flexibility, adhesives, and coatings; lubricant for aerosol valves, antifoaming agent, skin emollient, plasticizer in personal care products and cosmetics	Potential endocrine system disruptor
Butylbenzyl phthalate CAS#: 85-68-7 Formula: $C_{19}H_{20}O_4$ MW: 312		Plasticizer added to polyvinyl chloride to increase flexibility, adhesives, and coatings	Suspected carcinogen and neural toxicant; potential endocrine system disruptor
Bis(2-ethylhexyl) adipate CAS#: 103-23-1 Formula: $C_{22}H_{42}O_4$ MW: 370		Plasticizer added to flexible polyvinyl chloride products	Suspected carcinogen
Bis(2-ethylhexyl) phthalate CAS#: 117-81-7 Formula: $C_{24}H_{38}O_4$ MW: 390		Plasticizer in flexible polyvinyl chloride products; replacement for PCBs in dielectric fluids for electric capacitors	Potential endocrine system disruptor

Table 14. Triphenylphosphate: chemical structure, common uses, and toxicity.

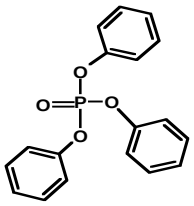
Compound Name	Chemical Structure	Common Uses	Toxicity
Triphenylphosphate CAS#: 115-86-6 Formula: $C_{18}H_{15}O_4P$ MW: 326		Flame retardant in plastic of video monitors and roofing materials; plasticizer in some pesticides, gasoline additives, synthetic motor oils, and nerve gas	Accumulates and magnifies in biological tissues, potential endocrine system disruptor; toxic to aquatic green algae

Table 15. Pesticides: chemical structures, common uses, and toxicity.

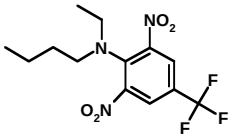
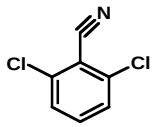
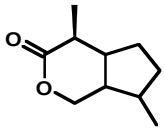
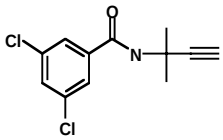
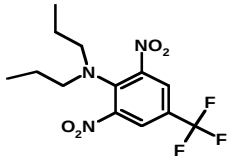
Compound Name	Chemical Structure	Common Uses	Toxicity
Benfluralin CAS#: 1861-40-1 Formula: $C_{13}H_{16}F_3N_3O_4$ MW: 335		Herbicide	Microtubule assembly inhibitor in plants; toxic to some aquatic species
2,6-Dichlorobenzonitrile CAS#: 1194-65-6 Formula: $C_7H_3Cl_2N$ MW: 171		Herbicide	Toxic to some aquatic species
Iridomyrmecin CAS#: 485-43-8 Formula: $C_{10}H_{16}O_2$ MW: 168		Insecticide and bactericide	Unknown
Propyzamide CAS#: 23950-58-5 Formula: $C_{12}H_{11}Cl_2NO$ MW: 255		Herbicide	Microtubule assembly inhibitor in plants; toxic to some aquatic species
Trifluralin CAS#: 1582-09-8 Formula: $C_{13}H_{16}F_3N_3O_4$ MW: 335		Herbicide	Microtubule assembly inhibitor in plants; toxic to some aquatic species

Table 16. Petroleum: chemical structures, common uses, and toxicity.

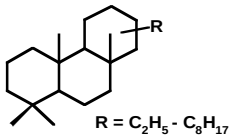
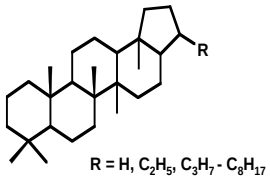
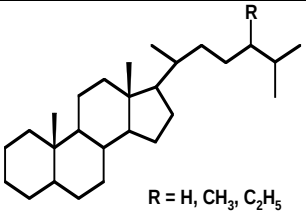
Compound Name	Chemical Structure	Common Uses	Toxicity
Extended tricyclic terpanes		Fossil fuel compounds; indicators of petroleum contamination when found in environmental samples	Unknown
Hopanes		Fossil fuel compounds; indicators of petroleum contamination when found in environmental samples	Unknown
Steranes		Fossil fuel compounds; indicators of petroleum contamination when found in environmental samples	Unknown

Table 17. Other synthetic compounds: chemical structures, common uses, and toxicity.

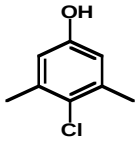
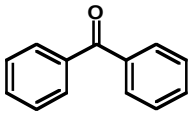
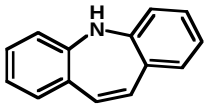
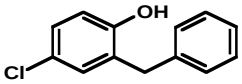
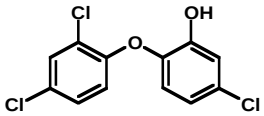
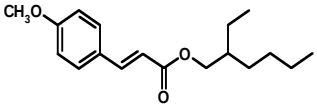
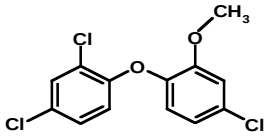
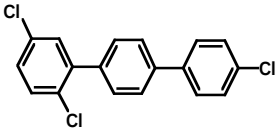
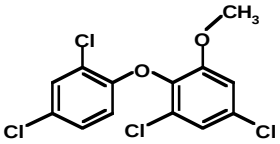
Compound Name	Chemical Structure	Common Uses	Toxicity
Chloroxylenol CAS#: 88-04-0 Formula: C_8H_9ClO MW: 156		Antiseptic and germicide, applied for mildew prevention	Unknown
Benzophenone CAS#: 119-61-9 Formula: $C_{13}H_{10}O$ MW: 182		Fixative in cosmetics and perfumes	Unknown
Imonostilbene CAS#: 256-96-2 Formula: $C_{14}H_{11}N$ MW: 193		Possible metabolite of carbamazepine an analgesic and anticonvulsant drug	Unknown
Chlorophene CAS#: 120-32-1 Formula: $C_{13}H_{11}ClO$ MW: 218		Antibacterial agent used in personal care products	Unknown
Triclosan CAS#: 3380-34-5 Formula: $C_{12}H_7Cl_3O_2$ MW: 288		Bacteriostat and preservative for cosmetics and detergents	Unknown
Octylmethoxy cinnamate CAS#: 5466-77-3 Formula: $C_{18}H_{26}O_3$ MW: 290		Active ingredient in sunscreens; acts as UV blocker	Unknown
Triclosan (methyl) CAS#: 4640-01-1 Formula: $C_{13}H_9Cl_3O_2$ MW: 302		Methylated analog of triclosan; bacterial alteration product	Unknown
2,4',5-Trichloro-p-terphenyl CAS#: 61576-93-0 Formula: $C_{18}H_{11}Cl_3$ MW: 334		Similar to PCBs; previously used as flame retardants in transformers; phased out	Bioaccumulates.
Triclosan (methyl-chloro) CAS#: Not available Formula: $C_{13}H_8Cl_4O_2$ MW: 336		Methylated and chlorinated analog of triclosan	Unknown

Table 18. Unidentified compounds in samples.

Characteristic fragments of mass spectra (relative intensities in %)										Medium
236	(28)	221	(66)	**143**	(100)	128	(43)	91	(66)	water
242	(15)	227	(45)	143	(25)	129	(15)	**116**	(100)	sediment
248	(77)	**233**	(100)	179	(43)	163	(54)	57	(65)	water
250	(10)	205	(14)	**193**	(100)	137	(10)	95	(12)	water
260	(8)	**245**	(100)	227	(22)	171	(32)	159	(36)	wastewater
266	(8)	**237**	(100)	181	(20)	167	(10)	57	(13)	water
274	(91)	259	(12)	**218**	(100)	202	(22)	189	(8)	water
298	(58)	**283**	(100)	241	(47)	91	(6)	57	(29)	water
312	(25)	**297**	(100)	241	(65)	57	(46)	155	(20)	water
314	(48)	299	(72)	**257**	(100)	109	(73)	57	(18)	water
318	(30)	**247**	(100)	219	(29)	147	(17)	57	(28)	water
326	(32)	311	(10)	270	(11)	**255**	(100)	57	(25)	water
340	(100)	325	(58)	283	(60)	241	(31)	57	(36)	water
343	(100)	286	(79)	272	(36)	232	(56)	57	(47)	water
359	(46)	302	(91)	**154**	(100)	91	(15)	57	(14)	water
364	(100)	349	(60)	181	(47)	153	(14)	57	(17)	water
365	(100)	308	(88)	159	(50)	91	(41)	57	(47)	water
368	(41)	**353**	(100)	297	(53)	241	(32)	57	(94)	water
377	(43)	**362**	(100)	172	(25)	145	(18)	57	(25)	water
386	(25)	**371**	(100)	294	(22)	91	(20)	119	(20)	sediment
388	(21)	371	(48)	245	(20)	99	(56)	**57**	(100)	water
405	(54)	**391**	(100)	119	(10)	103	(13)	91	(13)	water
410	(100)	395	(45)	206	(6)	162	(7)	57	(70)	water
418	(10)	403	(49)	**388**	(100)	119	(40)	103	(23)	water

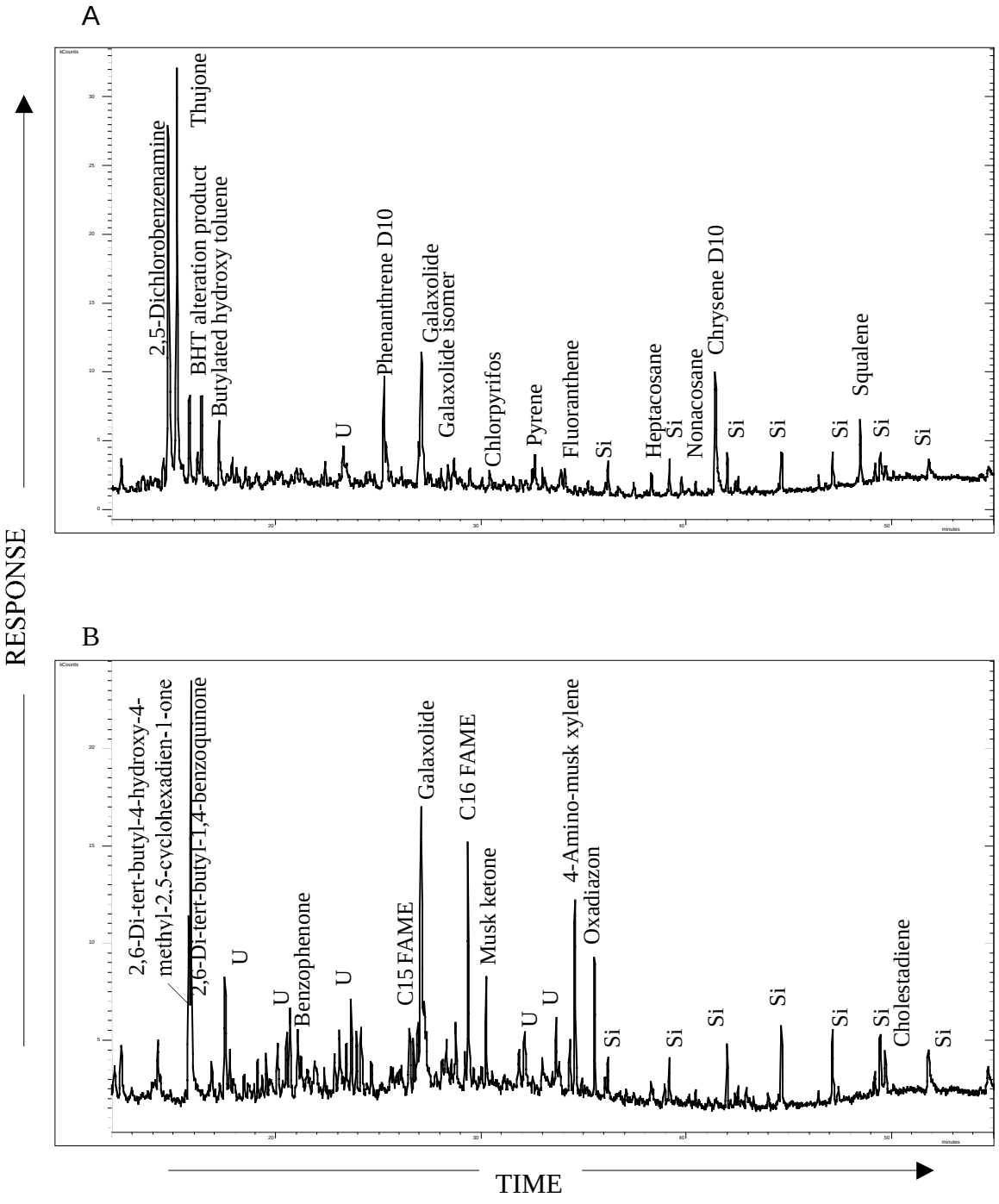
Base peak indicated by bold characters.
Highest mass corresponds to molecular ion M^+.

Table 19. Comparison of San Francisco Estuary water contaminants to USGS study results.

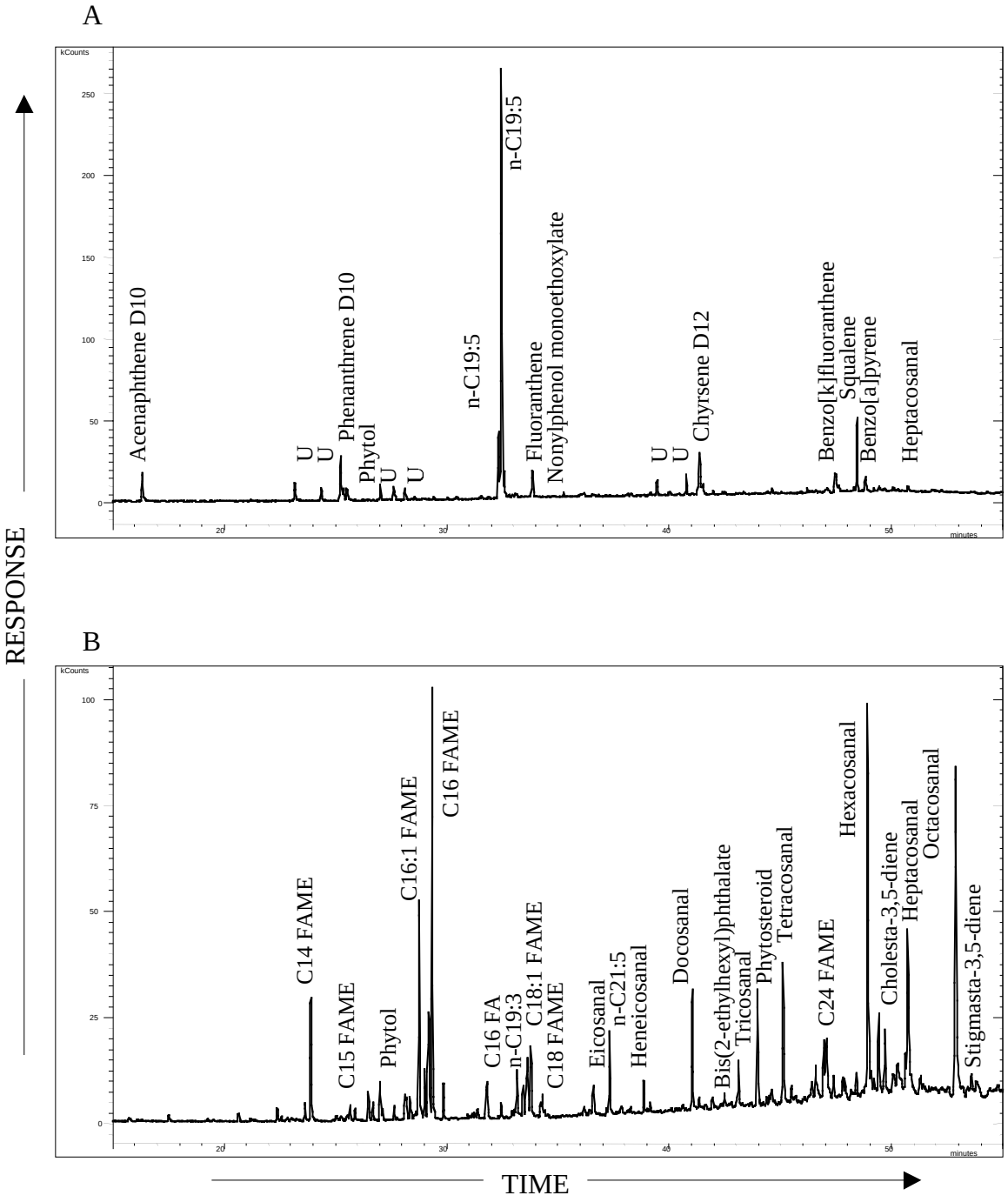
Compound	CAS#	USGS Study Max (µg/L)	USGS Study Med (µg/L)	This Study Max (ng/L)	Use
2,6-Di-tert-butyl-1,4-benzoquinone	719-22-2	0.46	0.13	1	Antioxidant
Anthracene	120-12-7	0.11	0.07	0.45[a]	PAH
Benzo[a]pyrene	50-32-8	0.24	0.04	ND[a]	PAH
Bis(2-ethylhexyl)adipate	103-23-1	10	3	0.7	Plasticizer
Bis(2-ethylhexyl)phthalate	117-81-7	20	7	7	Plasticizer
Butylated hydroxy toluene	128-37-0	0.1	0.1	2502	Antioxidant
cis-Chlordane	5103-71-9	0.1	0.02	29[ac]	Insecticide
Chlorpyrifos	2921-88-2	0.31	0.06	373[a]	Insecticide
Diazinon	333-41-5	0.35	0.07	1400[a]	Insecticide
Dieldrin	60-57-1	0.21	0.18	99[a]	Insecticide
Fluoranthene	206-44-0	1.2	0.04	8[a]	PAH
Naphthalene	91-20-3	0.08	0.02	ND[a]	PAH
p-Nonylphenol	251-545-23	40	0.8	19	Surfactant Metabolite
Phenanthrene	85-01-8	0.53	0.04	3.7[a]	PAH
Pyrene	129-00-0	0.84	0.05	8.5[a]	PAH
Triclosan	3380-34-5	2.3	0.14	0.3[b]	Disinfectant
Triphenylphosphate	115-86-6	0.22	0.04	1	Plasticizer

USGS Data derived from Kolpin *et al.* (2002).
[a]Routinely monitored by the San Francisco Estuary RMP (data are from 2000 results).
[b]Triclosan compared to total triclosan metabolites found in this study.
[c]cis-Chlordane compared to alpha-chlordane.
Abbreviations: CAS#, Chemical Abstracts Service Registry Number;
Max, maximum concentration; Med, median concentration; ND, not detected.

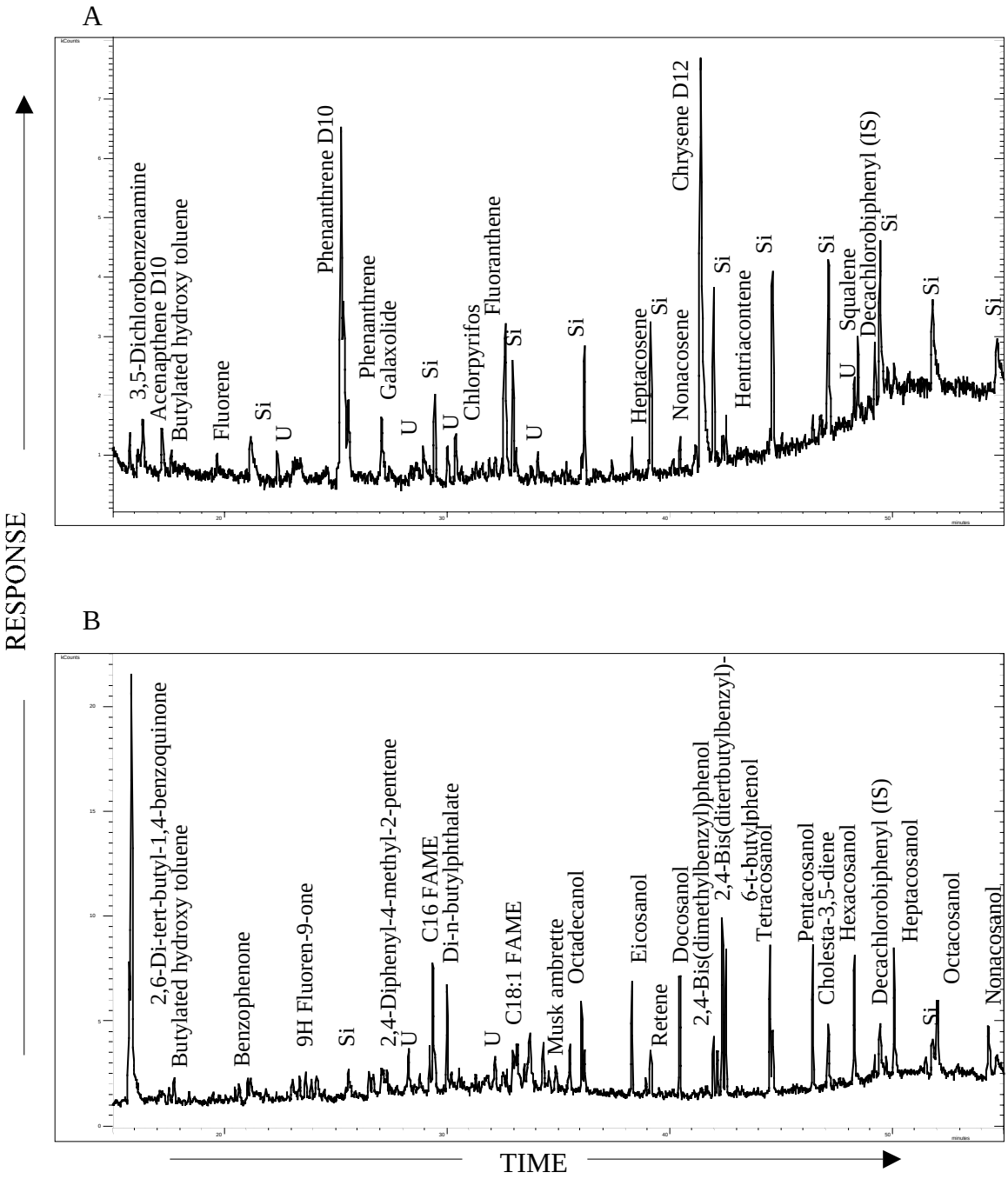
VII. APPENDICES



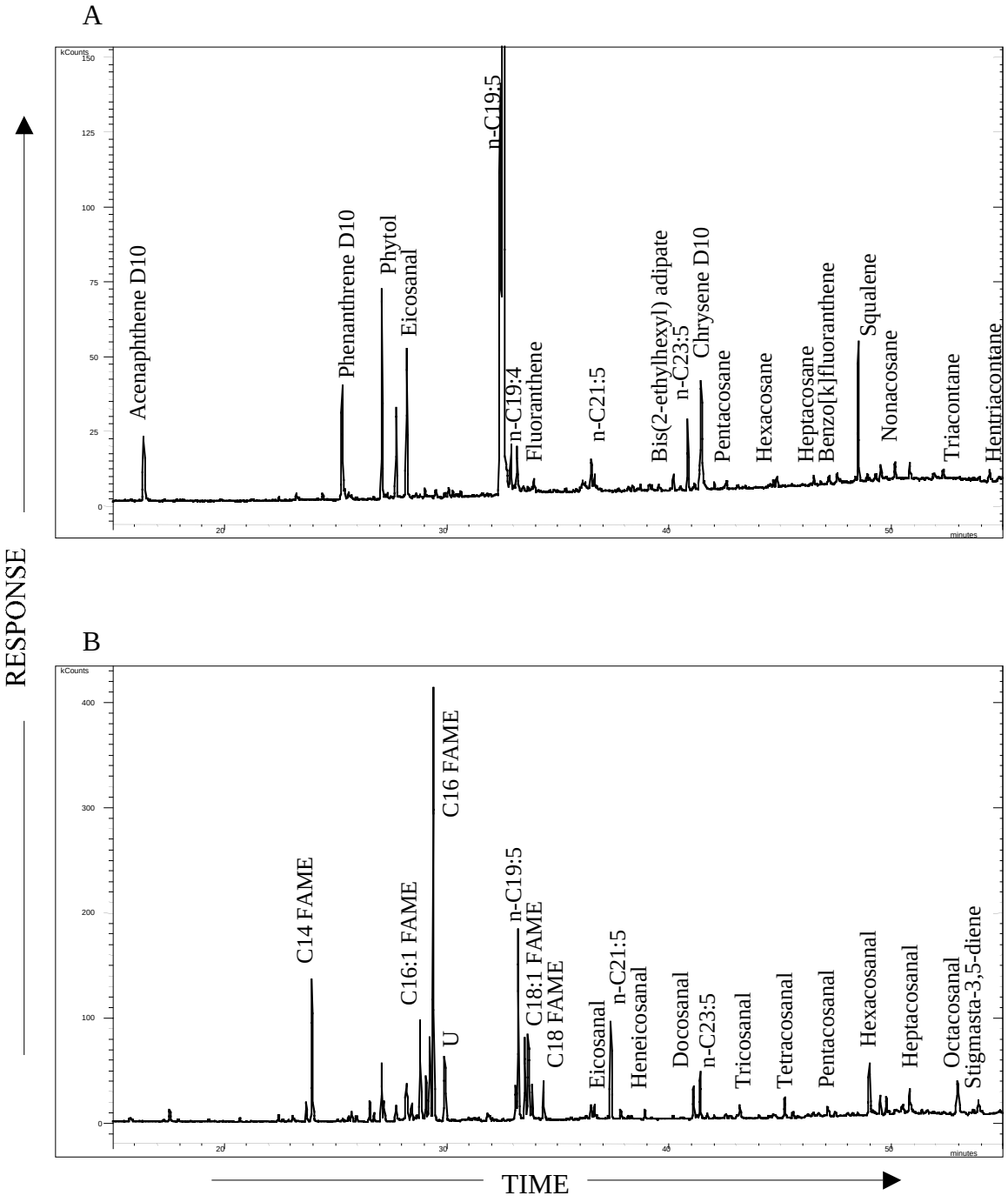
Appendix 1. GC-MS total ion current traces of a 1993 water sample from Dumbarton Bridge showing dissolved organic components: A) fraction 2, and B) fraction 3. Abbreviations: FAME = fatty acid methyl ester, Si = silicone, U = unknown.



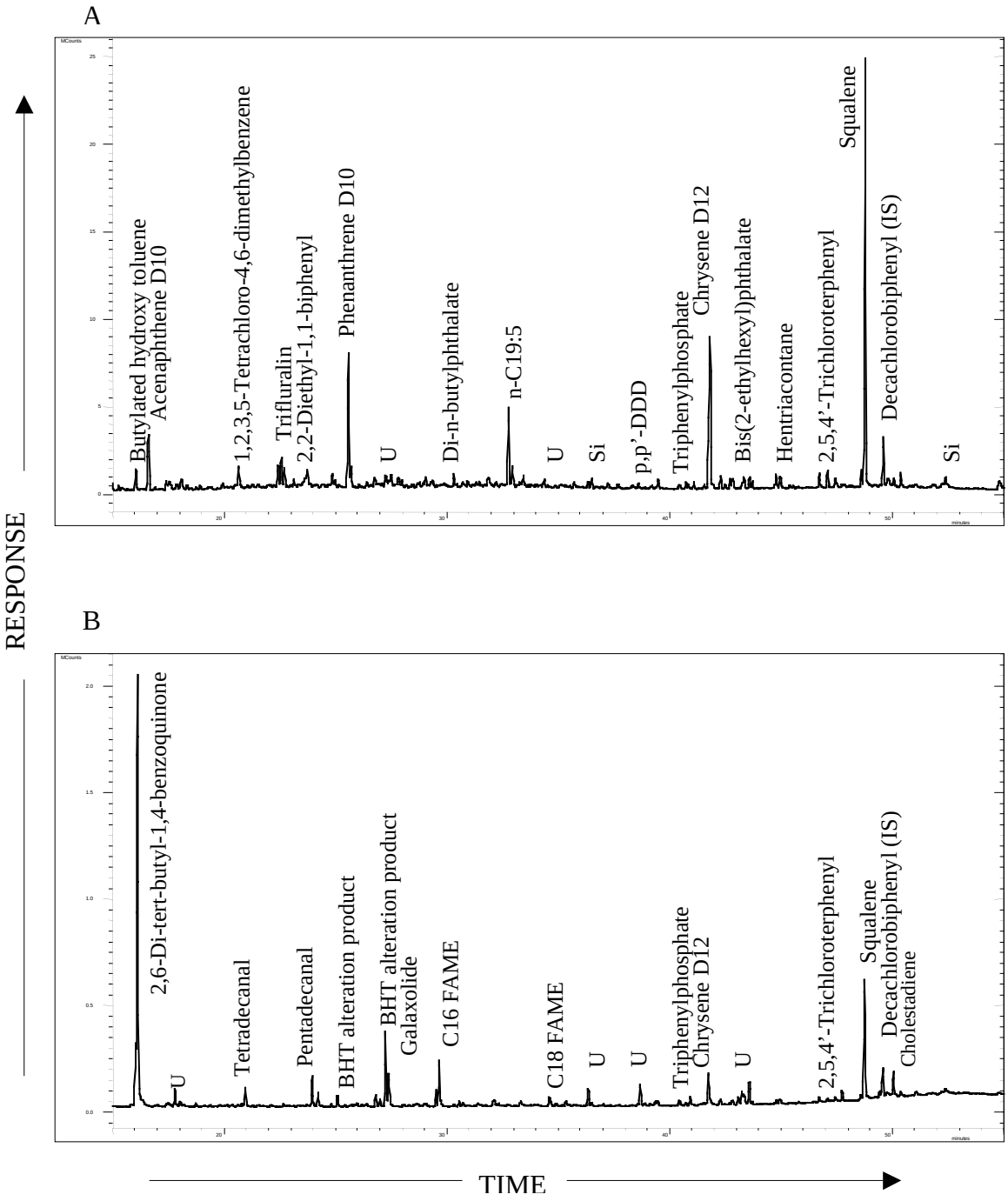
Appendix 2. GC-MS total ion current traces of a 1993 water sample from Dumbarton Bridge showing particulate organic components: A) fraction 2, and B) fraction 3. Abbreviations: FA = fatty acid, FAME = fatty acid methyl ester, Si = silicone, U = unknown.



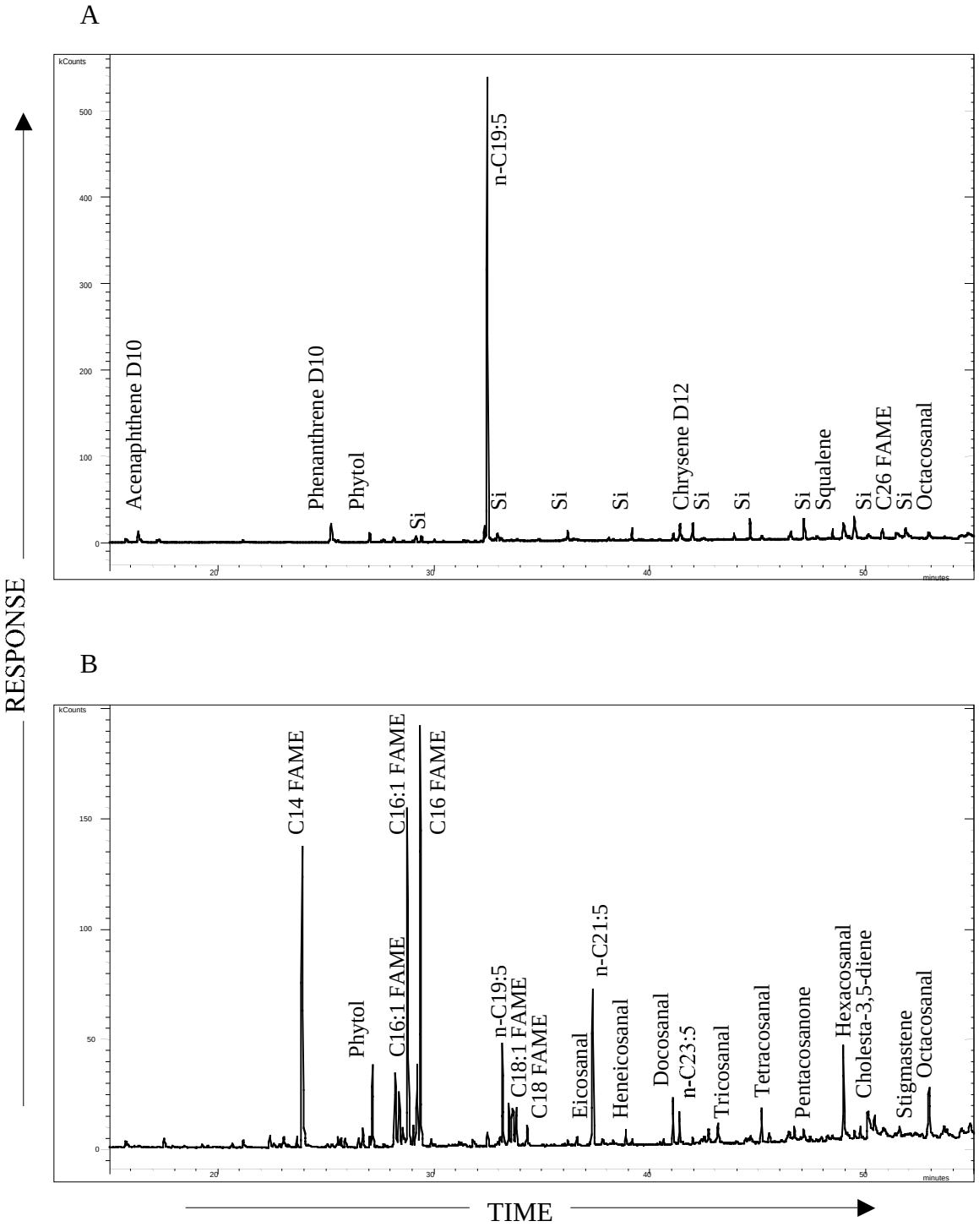
Appendix 3. GC-MS total ion current traces of a 1993 water sample from Yerba Buena Island showing dissolved organic components: A) fraction 2, and B) fraction 3. Abbreviations: FAME = fatty acid methyl ester, IS = internal standard, OH = n-alkanol, Si = silicone, U = unknown.



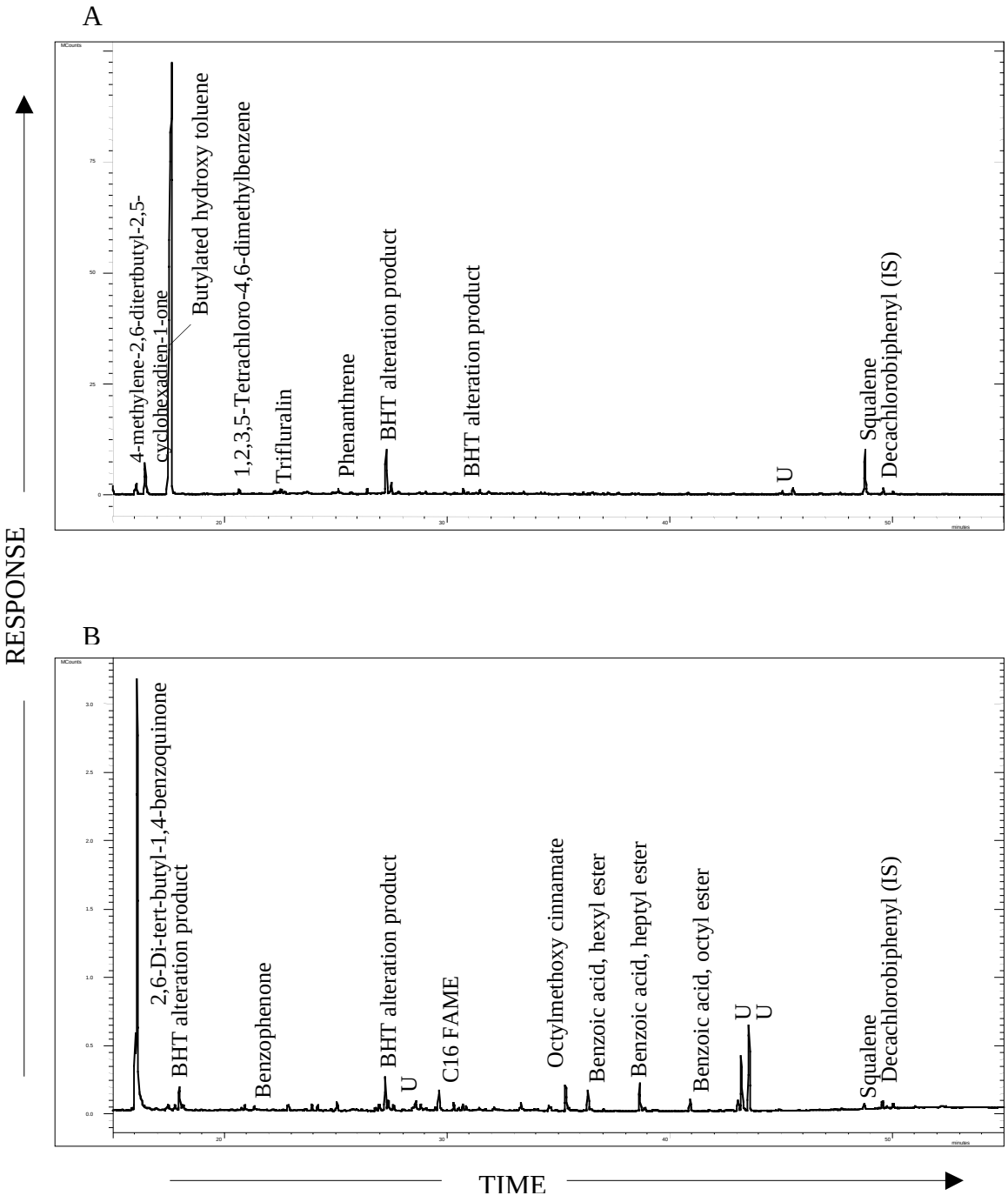
Appendix 4. GC-MS total ion current traces of a 1993 water sample from Yerba Buena Island showing particulate organic components: A) fraction 2 expanded, and B) fraction 3. Abbreviations: FA = fatty acid, FAME = fatty acid methyl ester, Si = silicone, U = unknown.



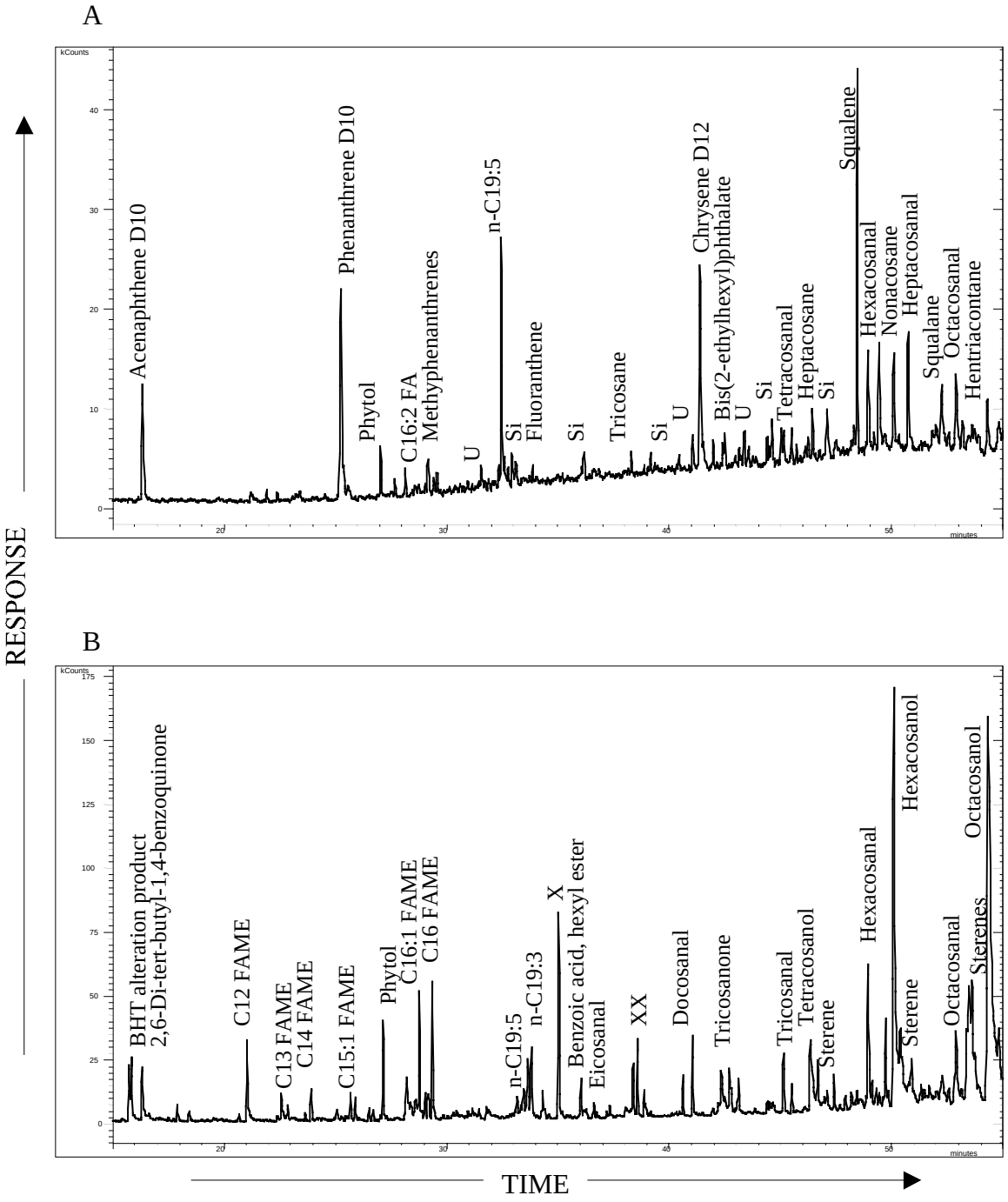
Appendix 5. GC-MS total ion current traces of a 1993 water sample from San Pablo Bay showing dissolved organic components: A) fraction 2, and B) fraction 3. Abbreviations: BHT = butylated hydroxytoluene, FAME = fatty acid methyl ester, IS = internal standard, Si = silicone, U = unknown.



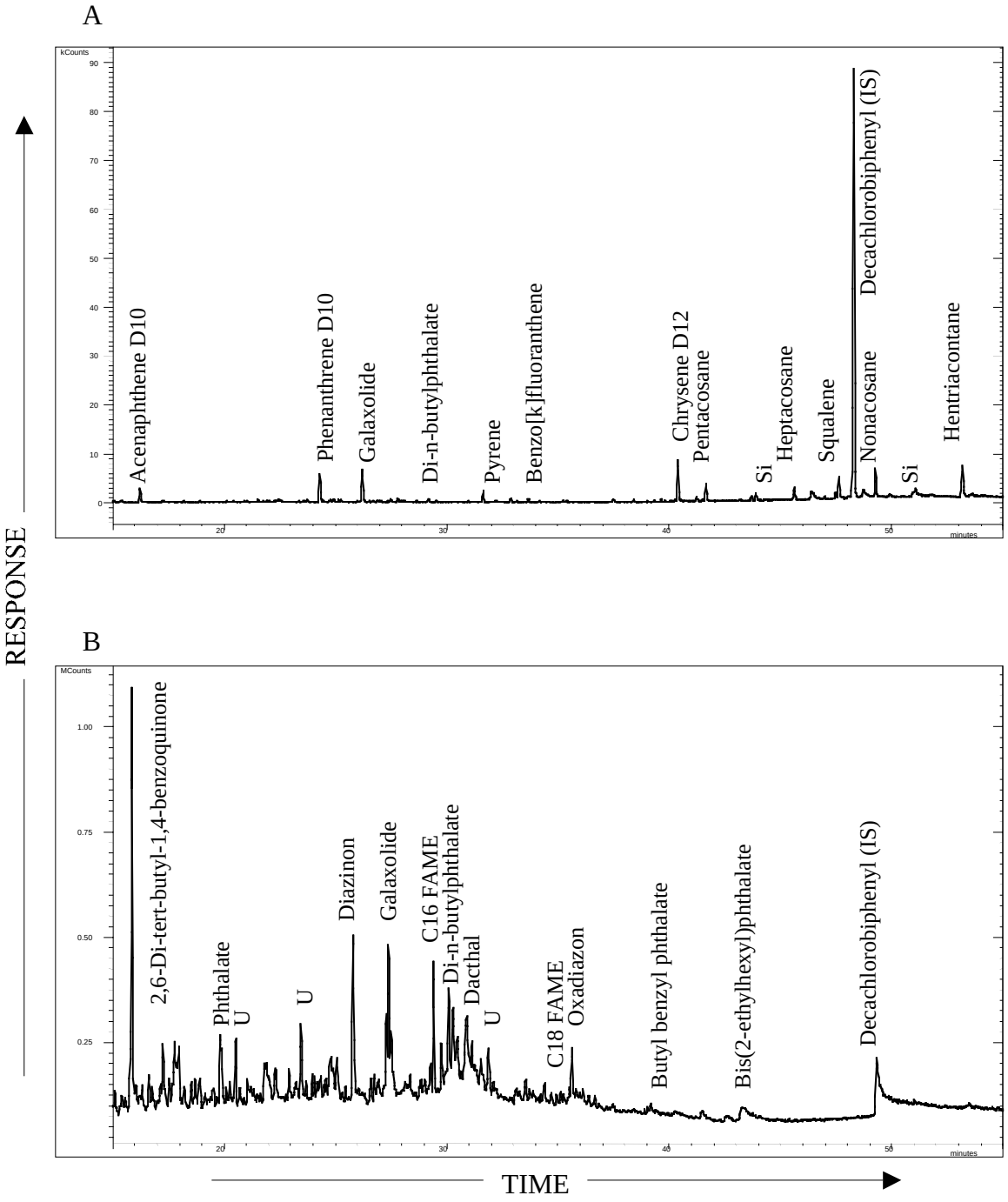
Appendix 6. GC-MS total ion current traces of a 1993 water sample from San Pablo Bay showing particulate organic components: A) fraction 2, and B) fraction 3. Abbreviations: FA = fatty acid, FAME = fatty acid methyl ester, Si = silicone, U = unknown.



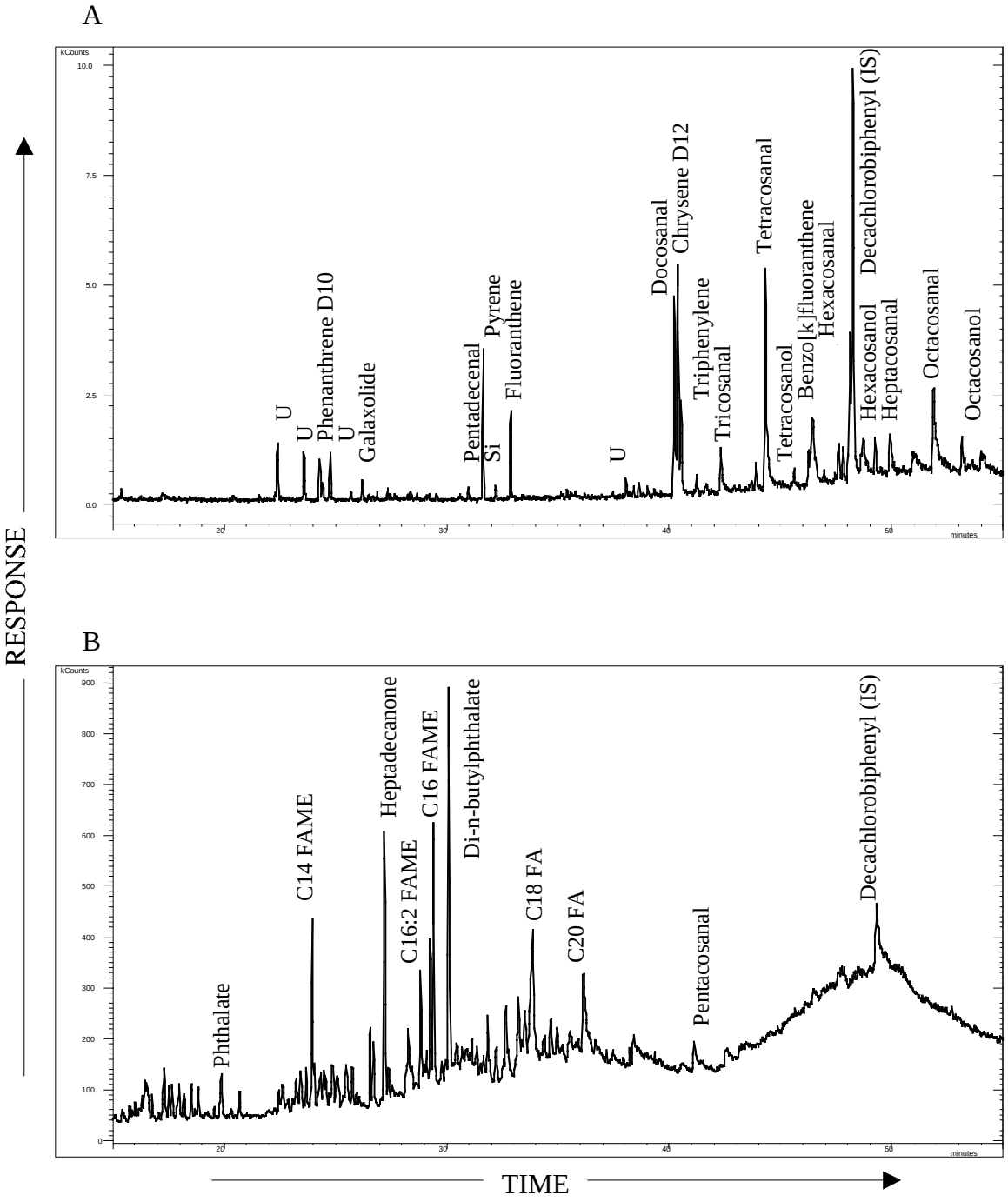
Appendix 7. GC-MS total ion current traces of a 1993 water sample from Grizzly Bay showing dissolved organic components: A) fraction 2, and B) fraction 3. Abbreviations: BHT = butylated hydroxytoluene, FAME = fatty acid methyl ester, IS = internal standard, Si = silicone, U = unknown.



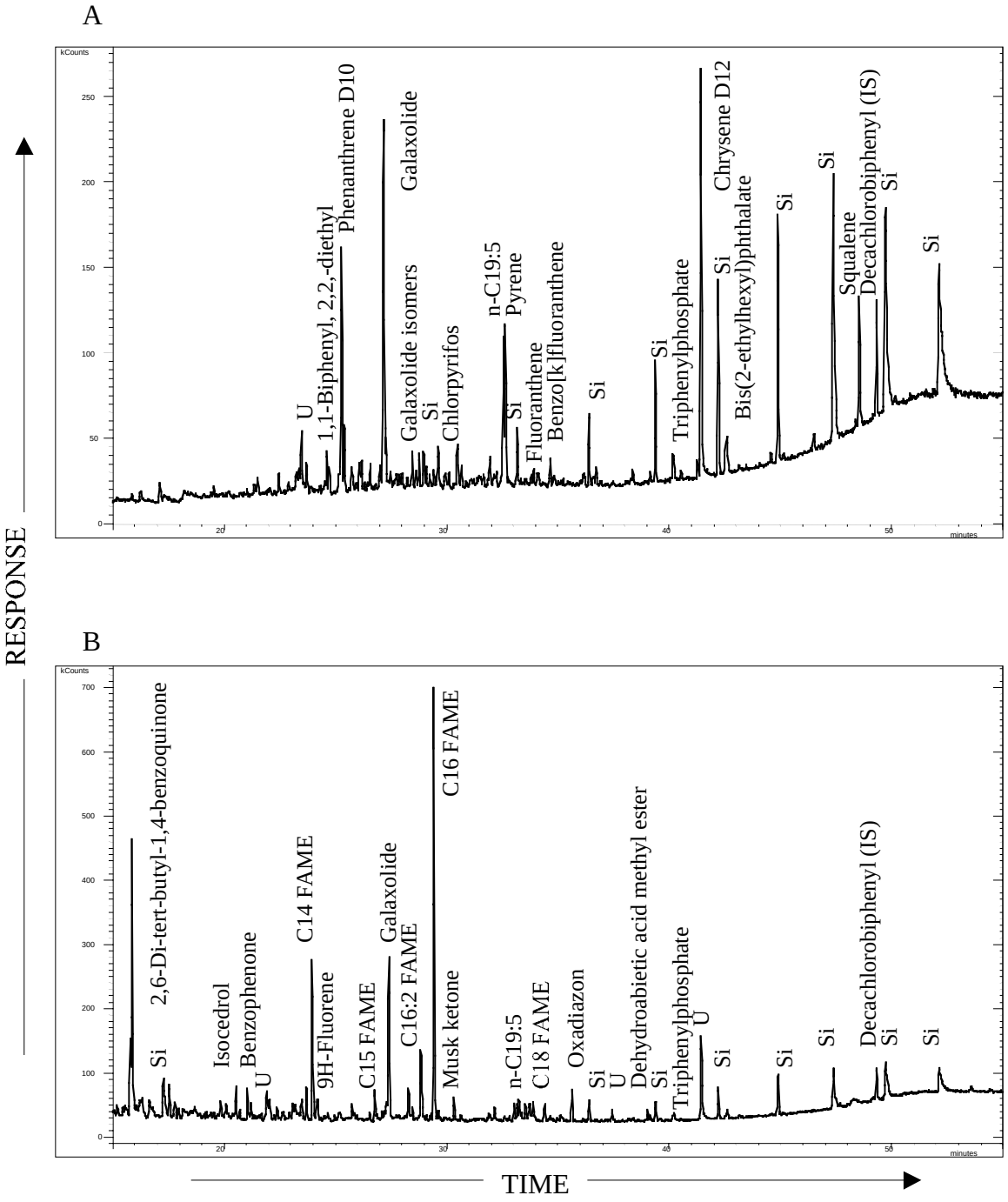
Appendix 8. GC-MS total ion current traces of a 1993 water sample from Grizzly Bay showing particulate organic components: A) fraction 2, and B) fraction 3. Abbreviations: BHT = butylated hydroxytoluene, FA = fatty acid, FAME = fatty acid methyl ester, Si = silicone, U = unknown, X = 2-propenoic acid, 3-(4-methoxyphenyl)-2-ethylhexyl ester, XX = 2-propenoic acid, 3-(4-methoxyphenyl)-2-ethylheptyl ester.



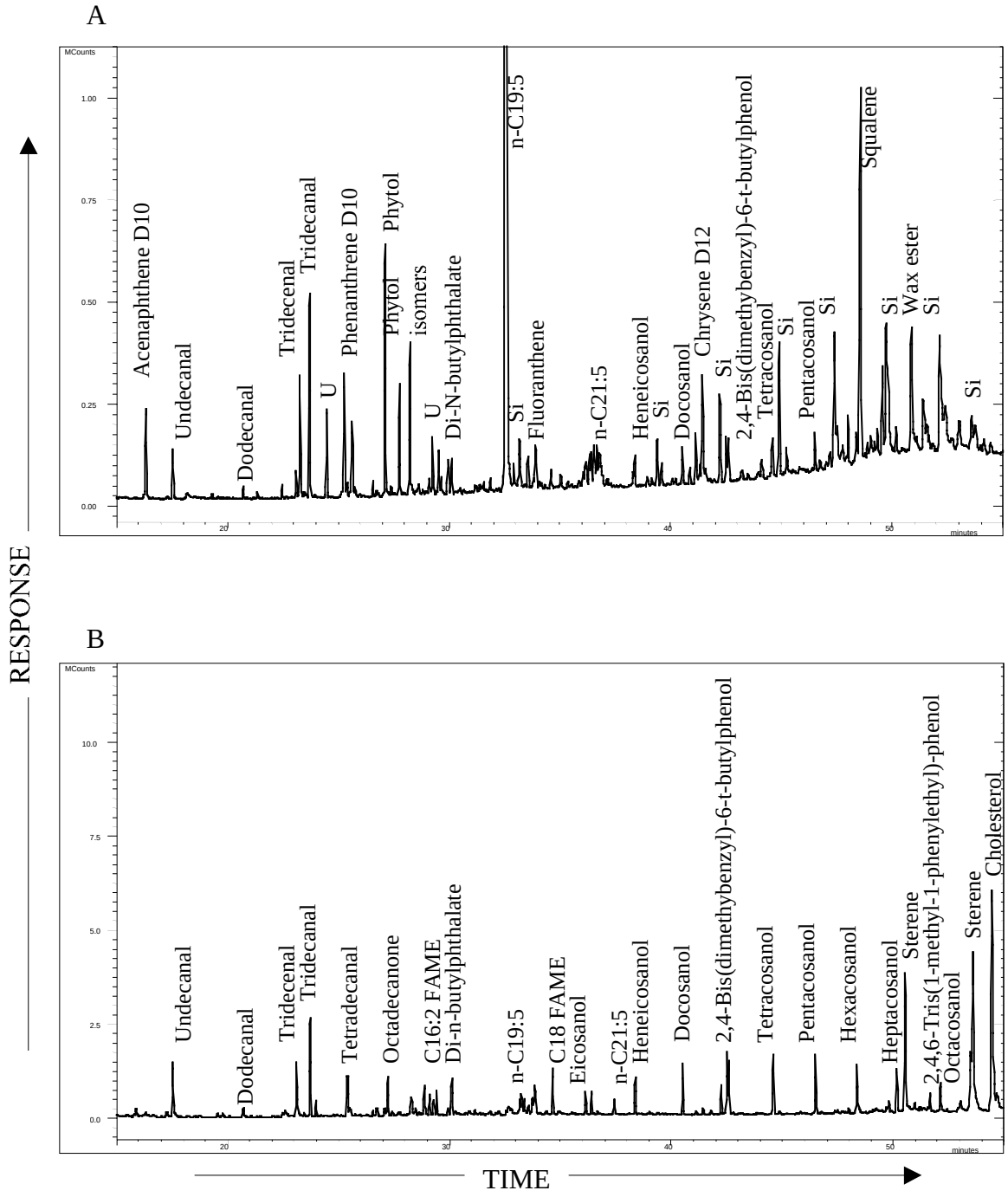
Appendix 9. GC-MS total ion current traces of a 1994 water sample from Dumbarton Bridge showing dissolved organic components: A) fraction 2, and B) fraction 3. Abbreviations: FAME = fatty acid methyl ester, IS = internal standard, Si = silicone, U= unknown.



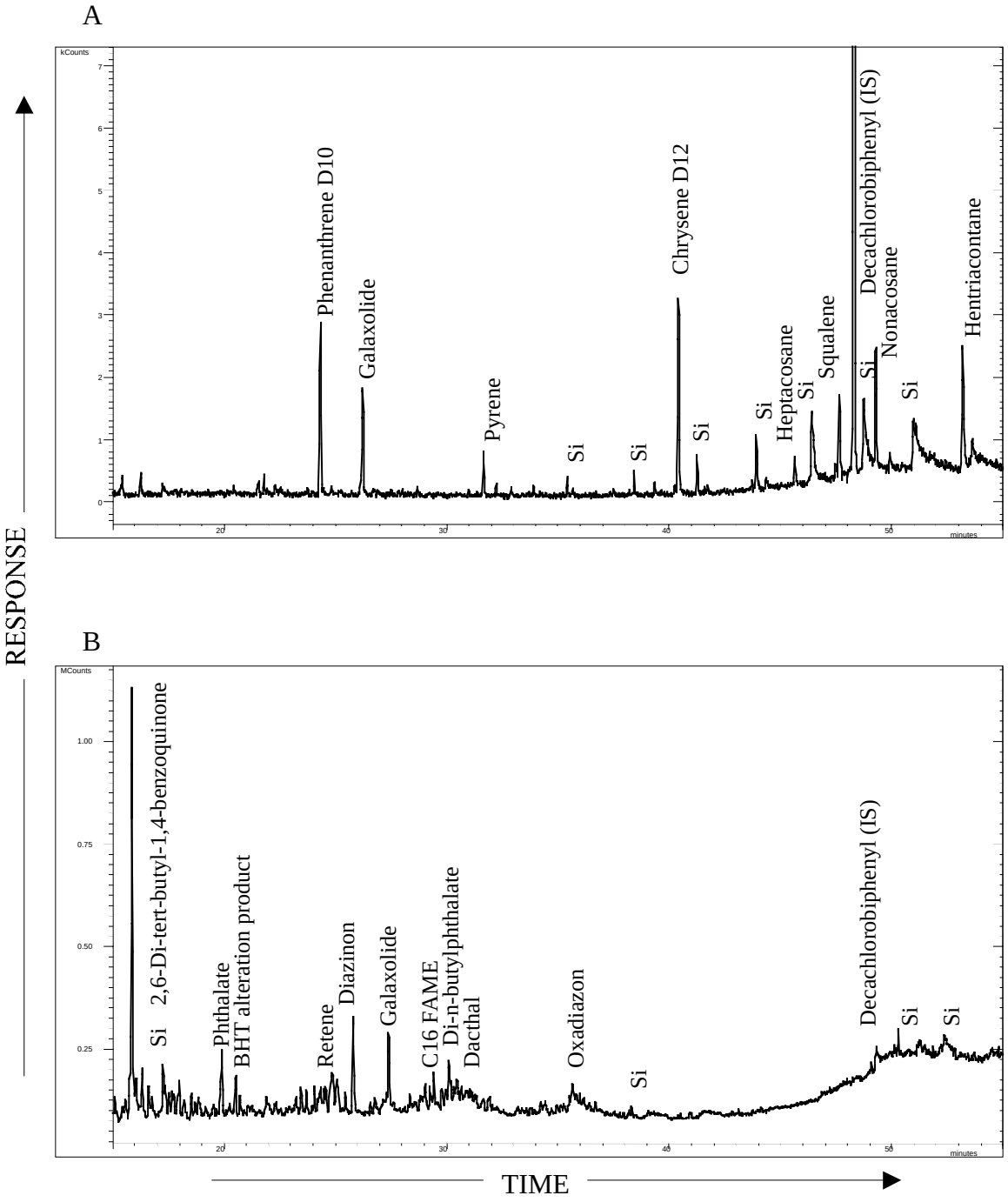
Appendix 10. GC-MS total ion current traces of a 1994 water sample from Dumbarton Bridge showing particulate organic components: A) fraction 2, and B) fraction 3. Abbreviations: FA = fatty acid, FAME = fatty acid methyl ester, IS = internal standard, Si = silicone, U = unknown.



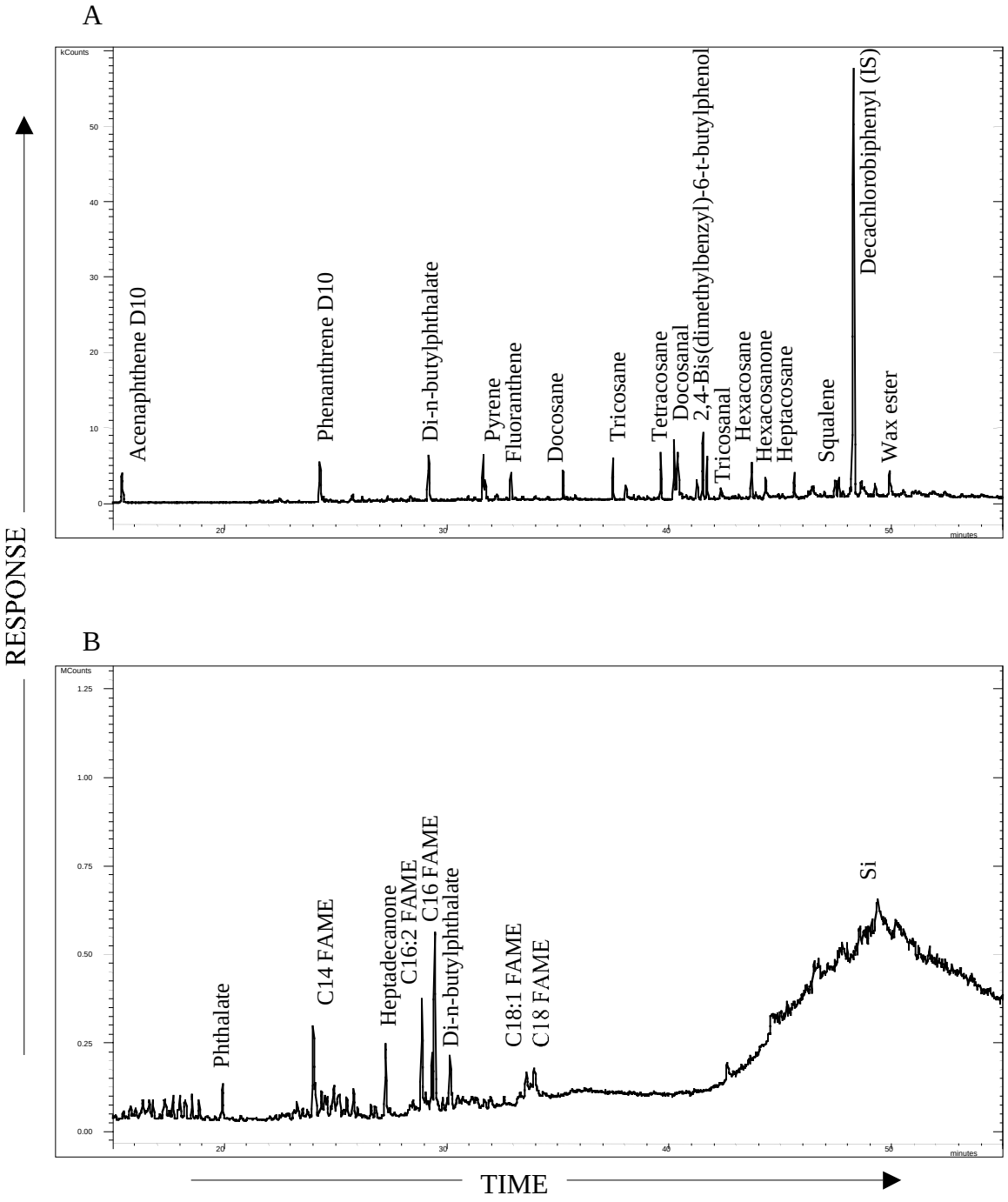
Appendix 11. GC-MS total ion current traces of a 1994 water sample from Yerba Buena Island showing dissolved organic components: A) fraction 2, and B) fraction 3. Abbreviations: FAME = fatty acid methyl ester, IS = internal standard, Si = silicone, U = unknown.



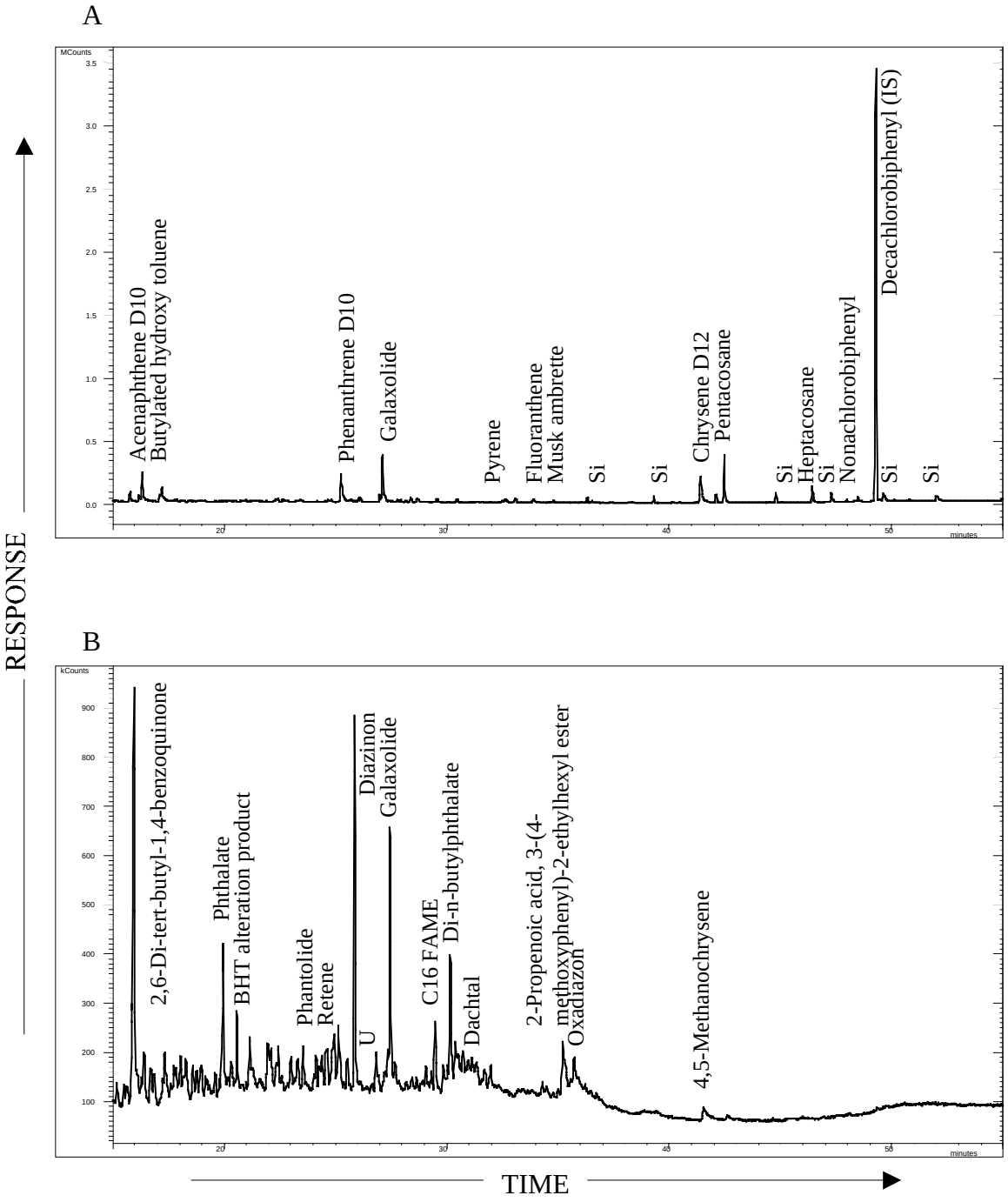
Appendix 12. GC-MS total ion current traces of a 1994 water sample from Yerba Buena Island showing particulate organic components: A) fraction 2 expanded, and B) fraction 3. Abbreviations: FA = fatty acid, FAME = fatty acid methyl ester, Si = silicone, U = unknown.



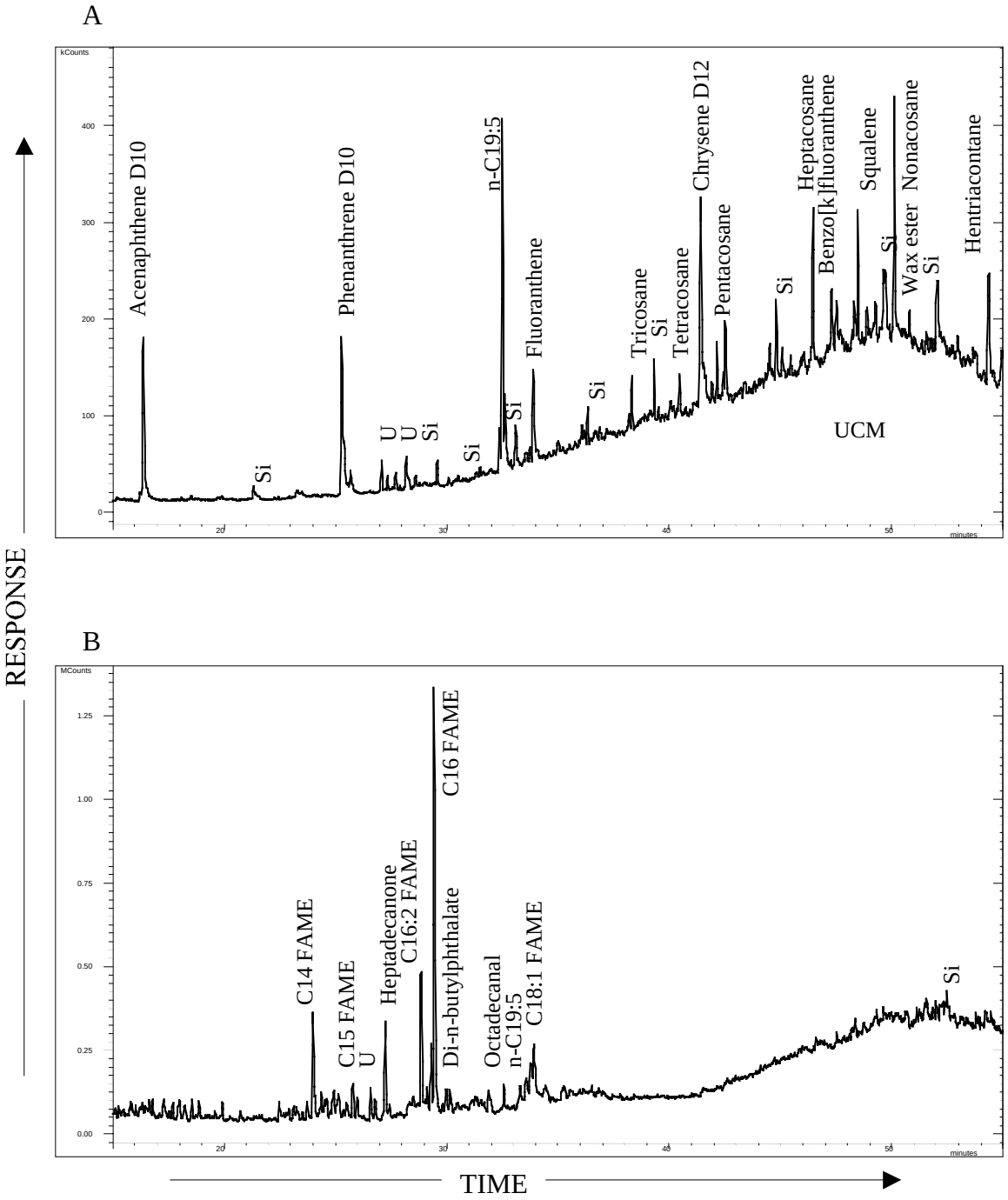
Appendix 13. GC-MS total ion current traces of a 1994 water sample from San Pablo Bay showing dissolved organic components: A) fraction 2 expanded, and B) fraction 3. Abbreviations: BHT = butylated hydroxytoluene, FAME = fatty acid methyl ester, IS = internal standard, Si = silicone, U = unknown.



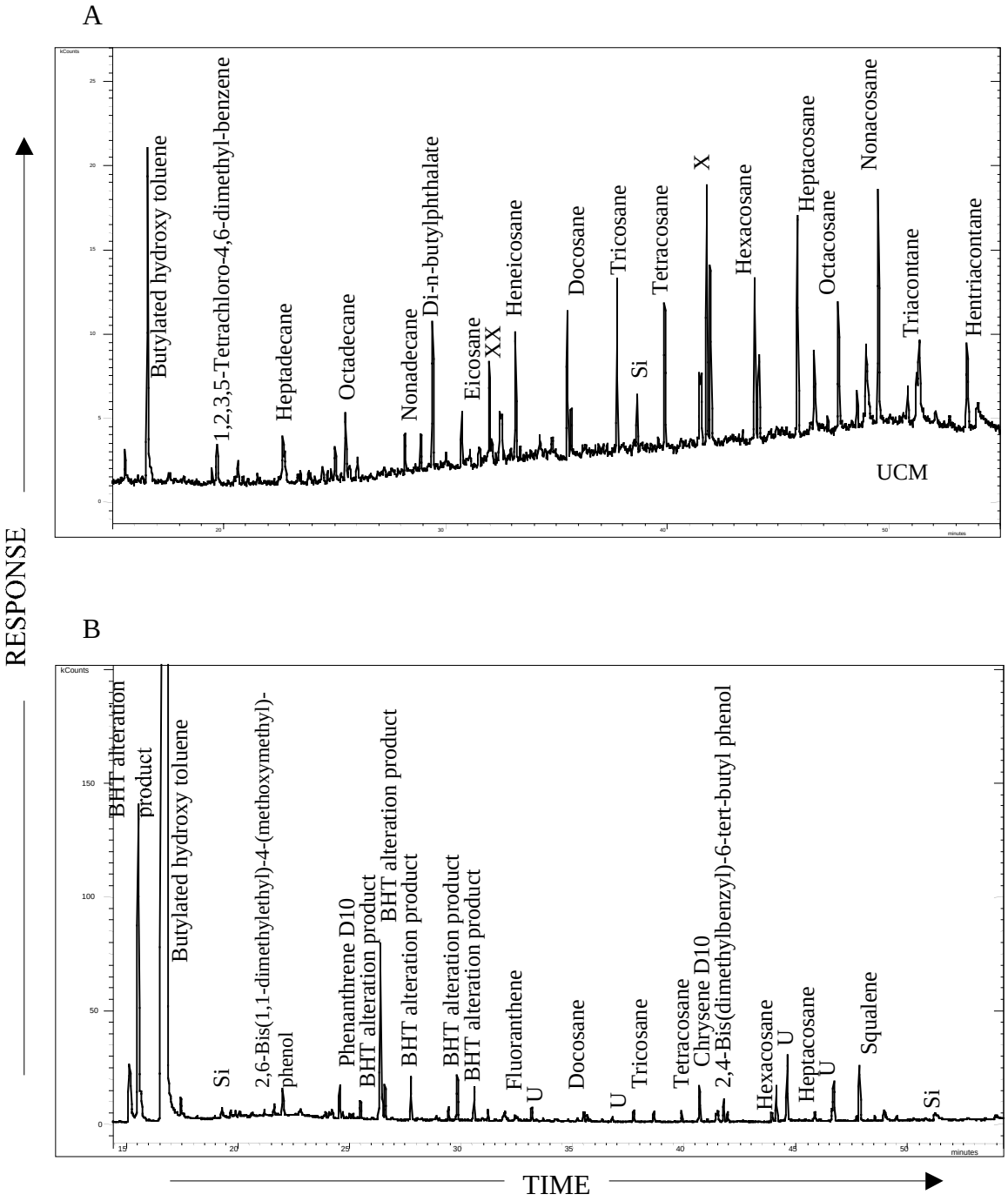
Appendix 14. GC-MS total ion current traces of a 1994 water sample from San Pablo Bay showing particulate organic components: A) fraction 2, and B) fraction 3. Abbreviations: FAME = fatty acid methyl ester, IS = internal standard, Si = silicone, U = unknown.



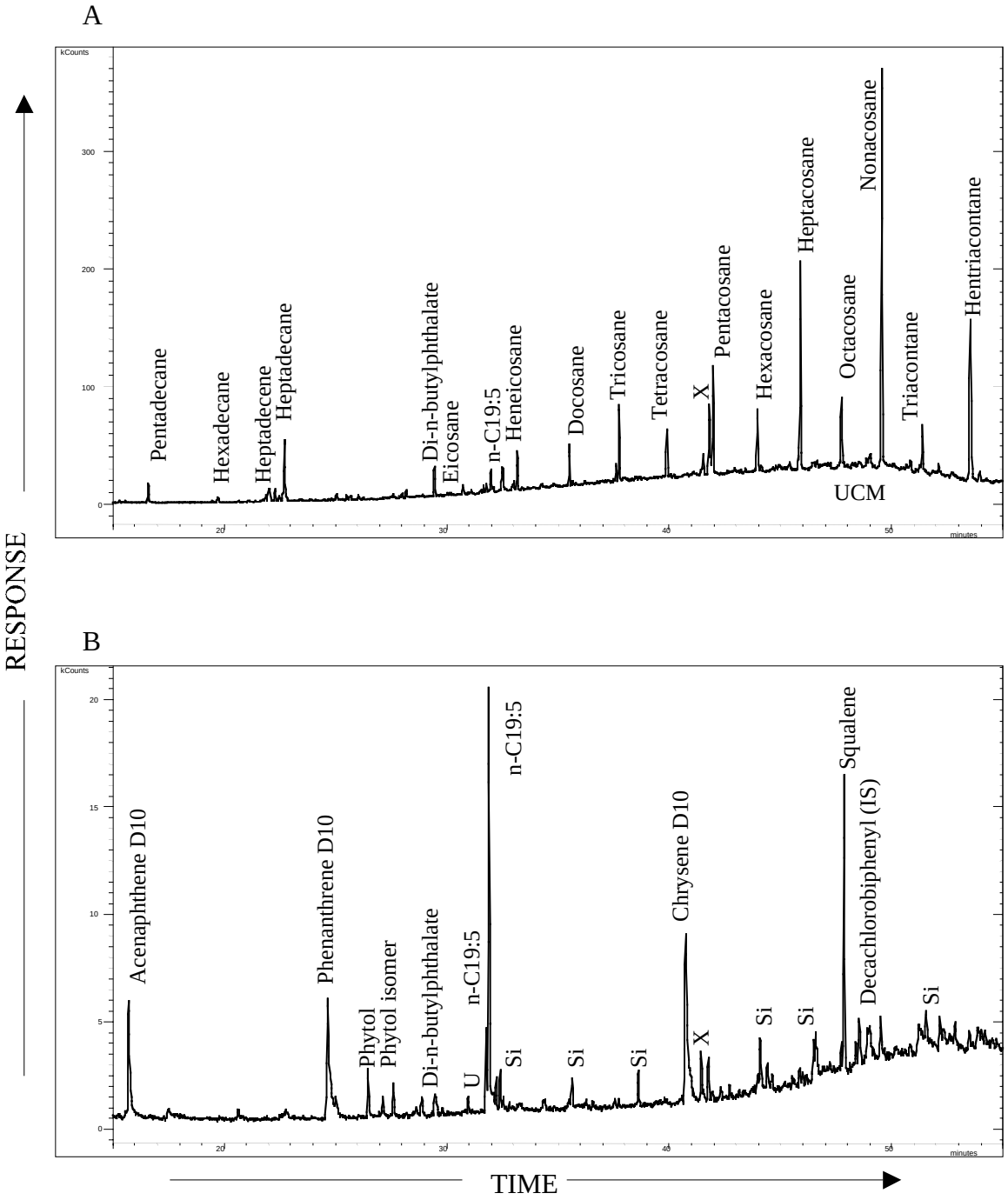
Appendix 15. GC-MS total ion current traces of a 1994 water sample from Grizzly Bay showing dissolved organic components: A) fraction 2, and B) fraction 3. Abbreviations: BHT = butylated hydroxytoluene, FAME = fatty acid methyl ester, IS = internal standard, Si = silicone, U = unknown.



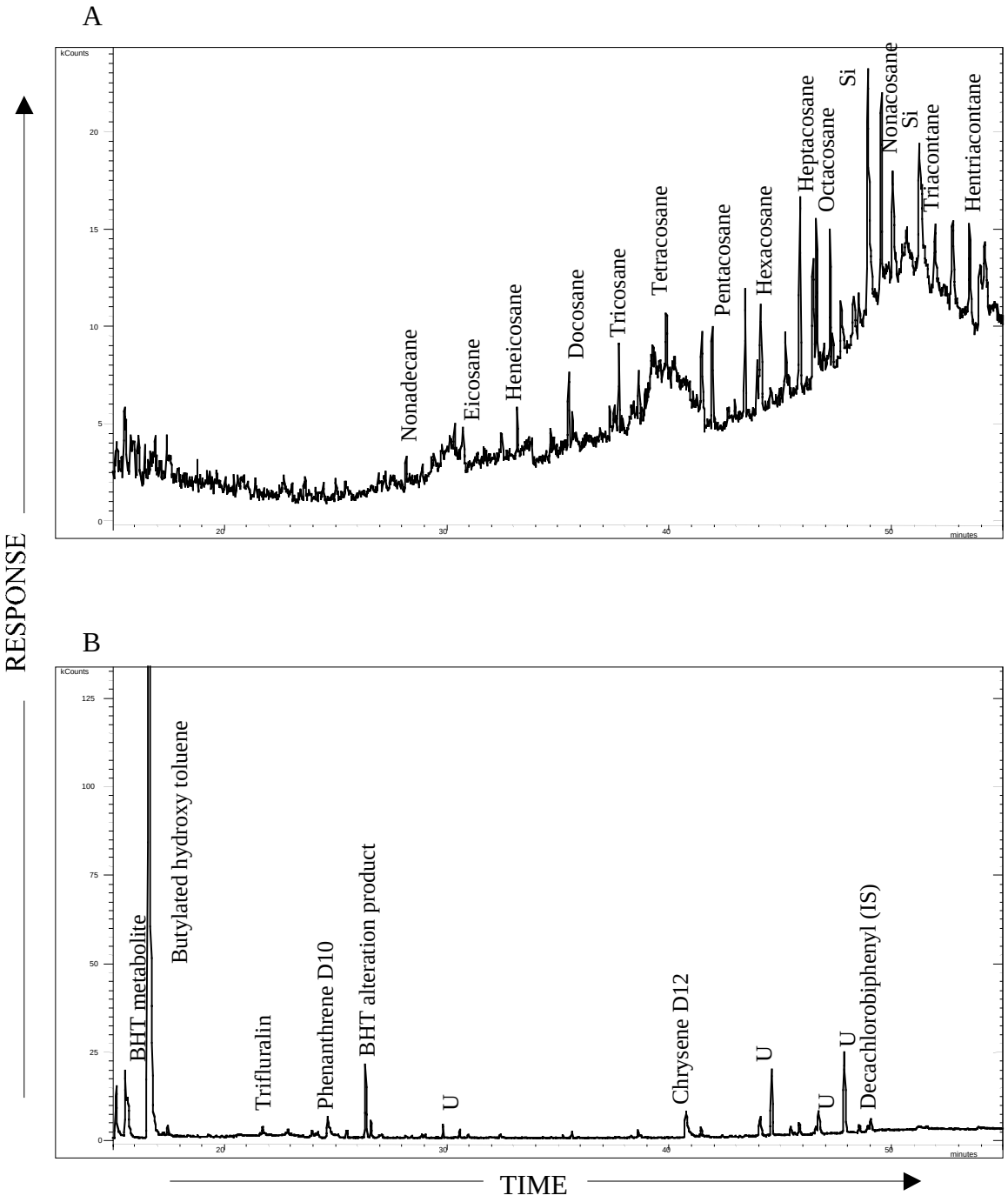
Appendix 16. GC-MS total ion current traces of a 1994 water sample from Grizzly Bay showing particulate organic components: A) fraction 2, and B) fraction 3. Abbreviations: FAME = fatty acid methyl ester, Si = silicone, U = unknown, UCM = unresolved complex mixture.



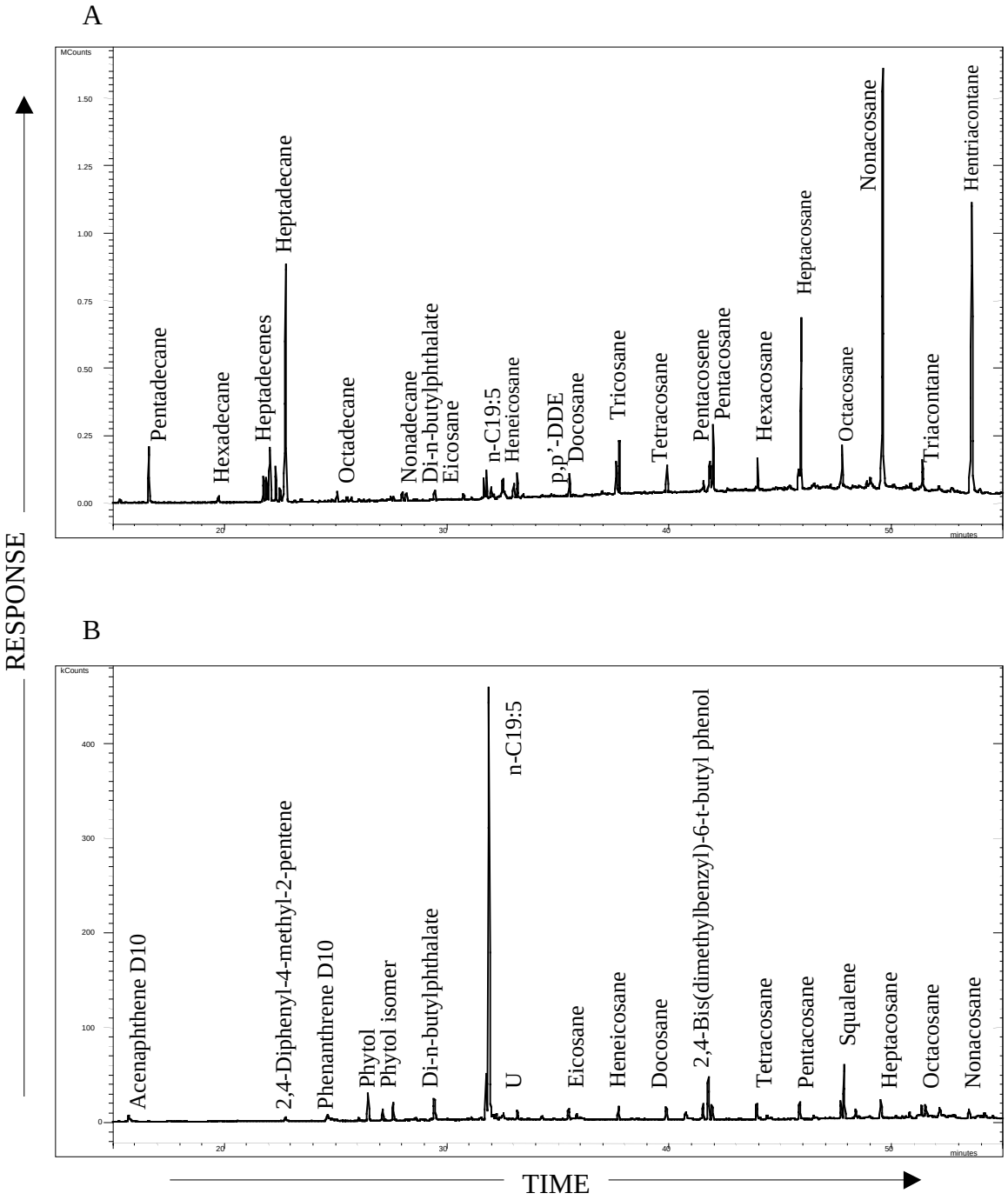
Appendix 17. GC-MS total ion current traces of a 1993 river water sample from Sacramento River, Rio Vista, showing dissolved organic components: A) fraction 1, and B) fraction 2 expanded. Abbreviations: BHT = butylated hydroxytoluene, Si = silicone; U = unknown, UCM = unresolved complex mixture, X = 2,4-Bis(dimethylbenzyl)-6-tert-butyl-phenol, XX = 2,6-Bis(1,1-dimethyl)-4-(1-methyl-1-phenylmethyl)-phenol.



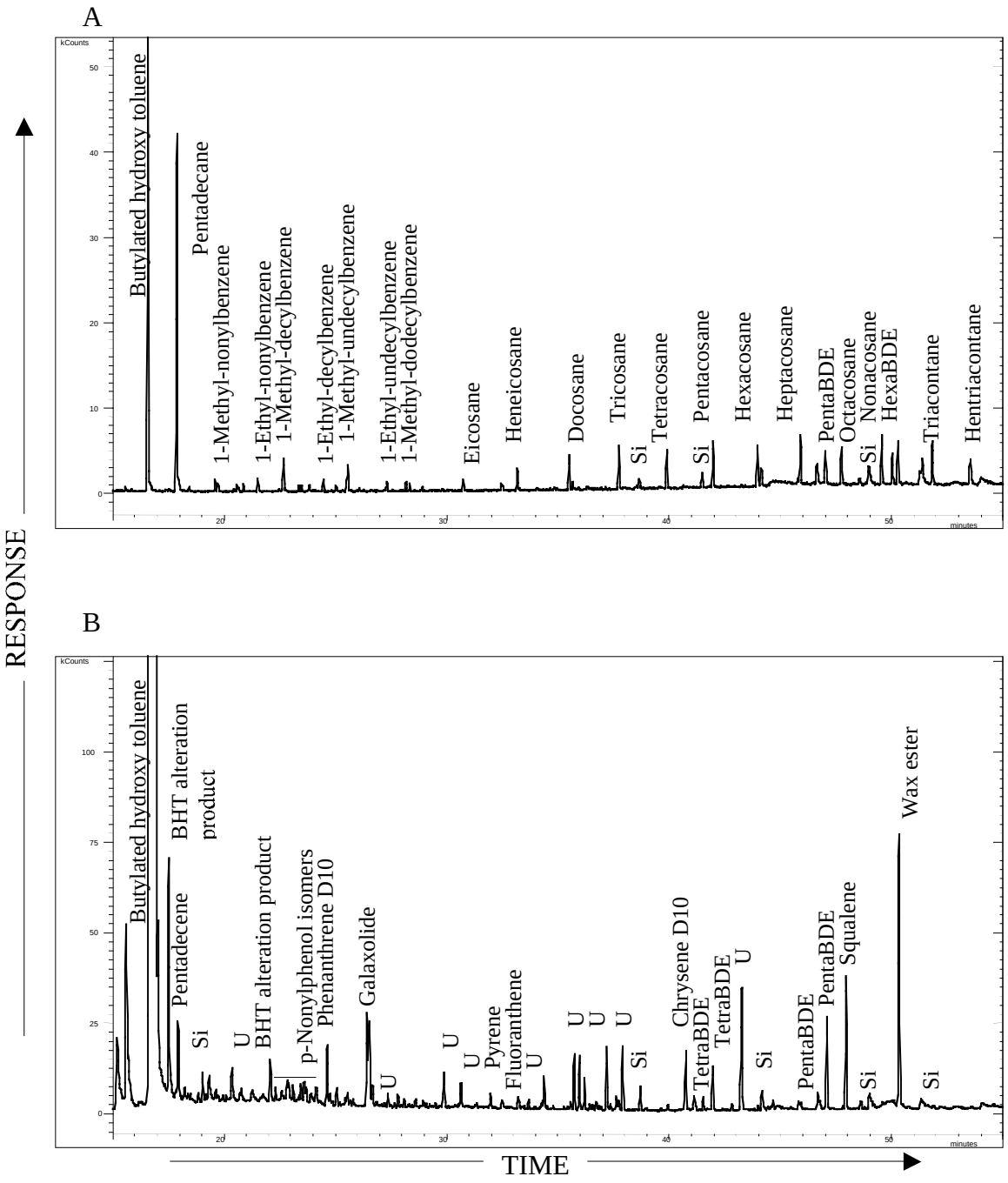
Appendix 18. GC-MS total ion current traces of a 1993 river water sample from Sacramento River, Rio Vista, showing particulate organic components: A) fraction 1, and B) fraction 2. Abbreviations: FA = fatty acid, IS = internal standard, Si = silicone, U = unknown, UCM = unresolved complex mixture, X = 2,4-bis(dimethylbenzyl)-6-t-butyl-phenol.



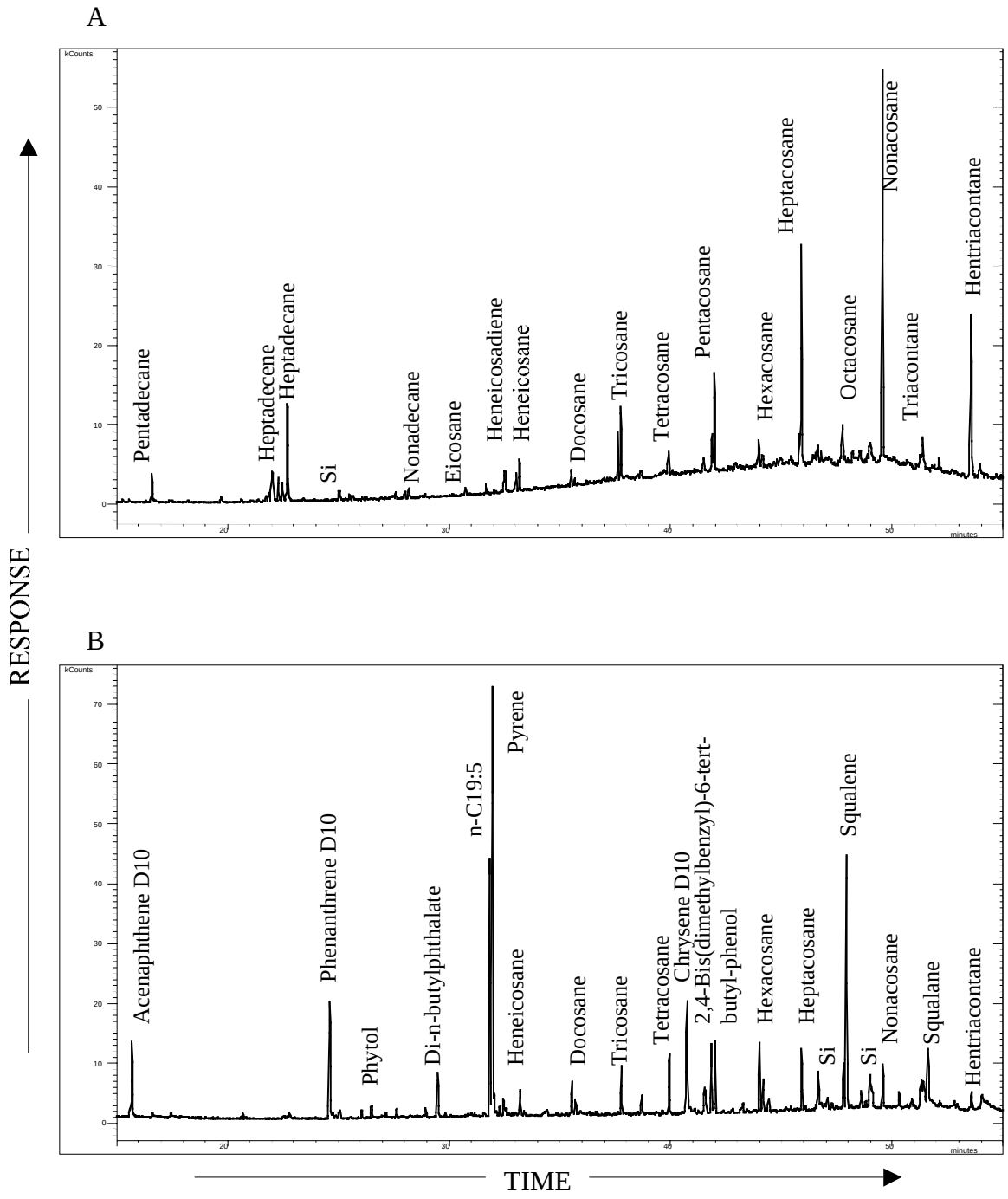
Appendix 19. GC-MS total ion current traces of a 1993 river water sample from San Joaquin River, Manteca, showing dissolved organic components: A) fraction 1, and B) fraction 2 expanded. Abbreviations: BHT = butylated hydroxytoluene, IS = internal standard, Si = silicone, U = unknown.



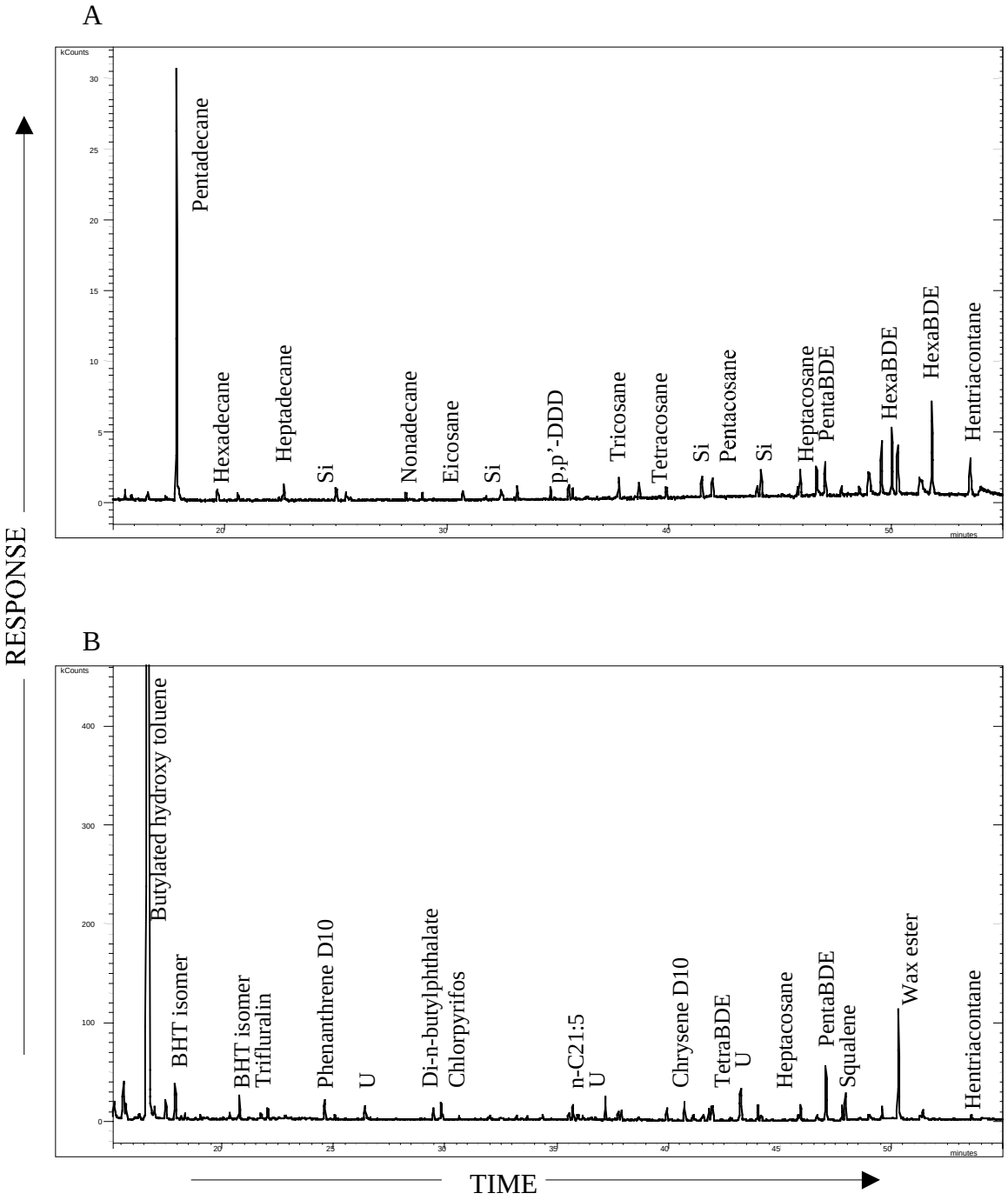
Appendix 20. GC-MS total ion current traces of a 1993 river water sample from San Joaquin River, Manteca, showing particulate organic components: A) fraction 1, and B) fraction 2. Abbreviation: FA = fatty acid, U = unknown.



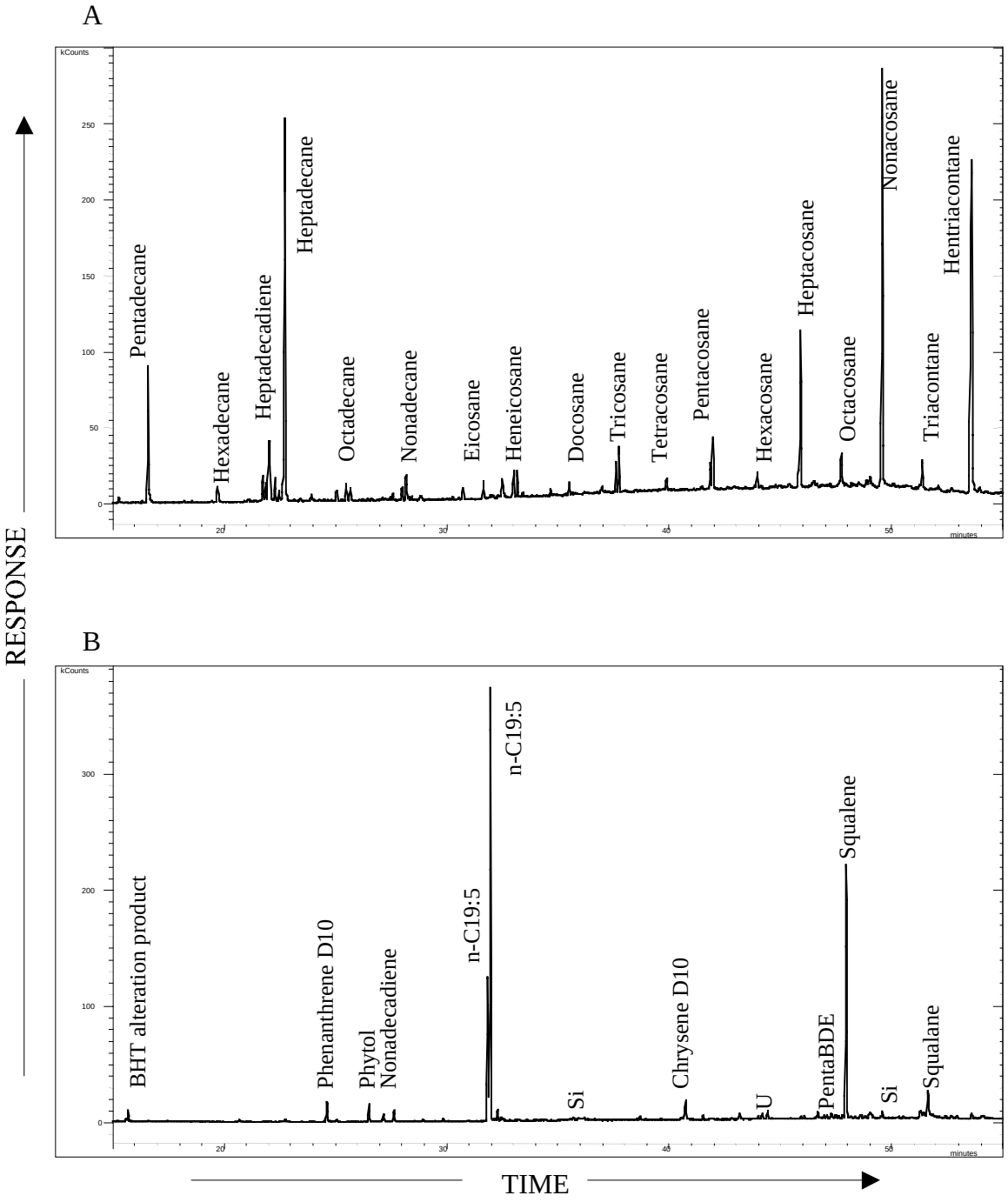
Appendix 21. GC-MS total ion current traces of a 1994 river water sample from Sacramento River, Rio Vista, showing dissolved organic components: A) fraction 1, and B) fraction 2 expanded. Abbreviations: BDE = bromo diphenyl ether, BHT = butylated hydroxytoluene, Si = silicone, U = unknown.



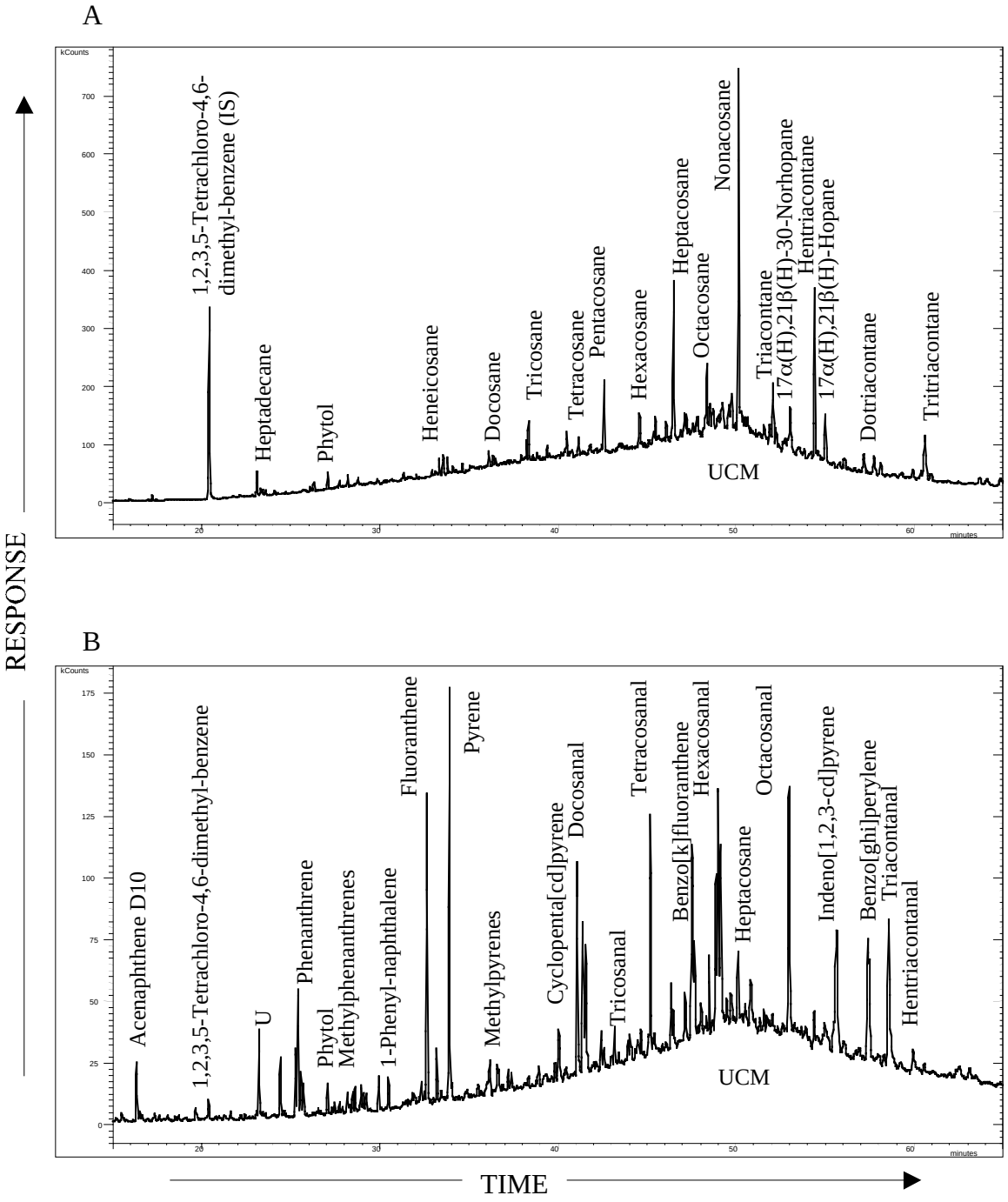
Appendix 22. GC-MS total ion current traces of a 1994 river water sample from Sacramento River, Rio Vista, showing particulate organic components: A) fraction 1, and B) fraction 2. Abbreviations: BDE = bromo diphenyl ether, FA = fatty acid, Si = silicone, U = unknown.



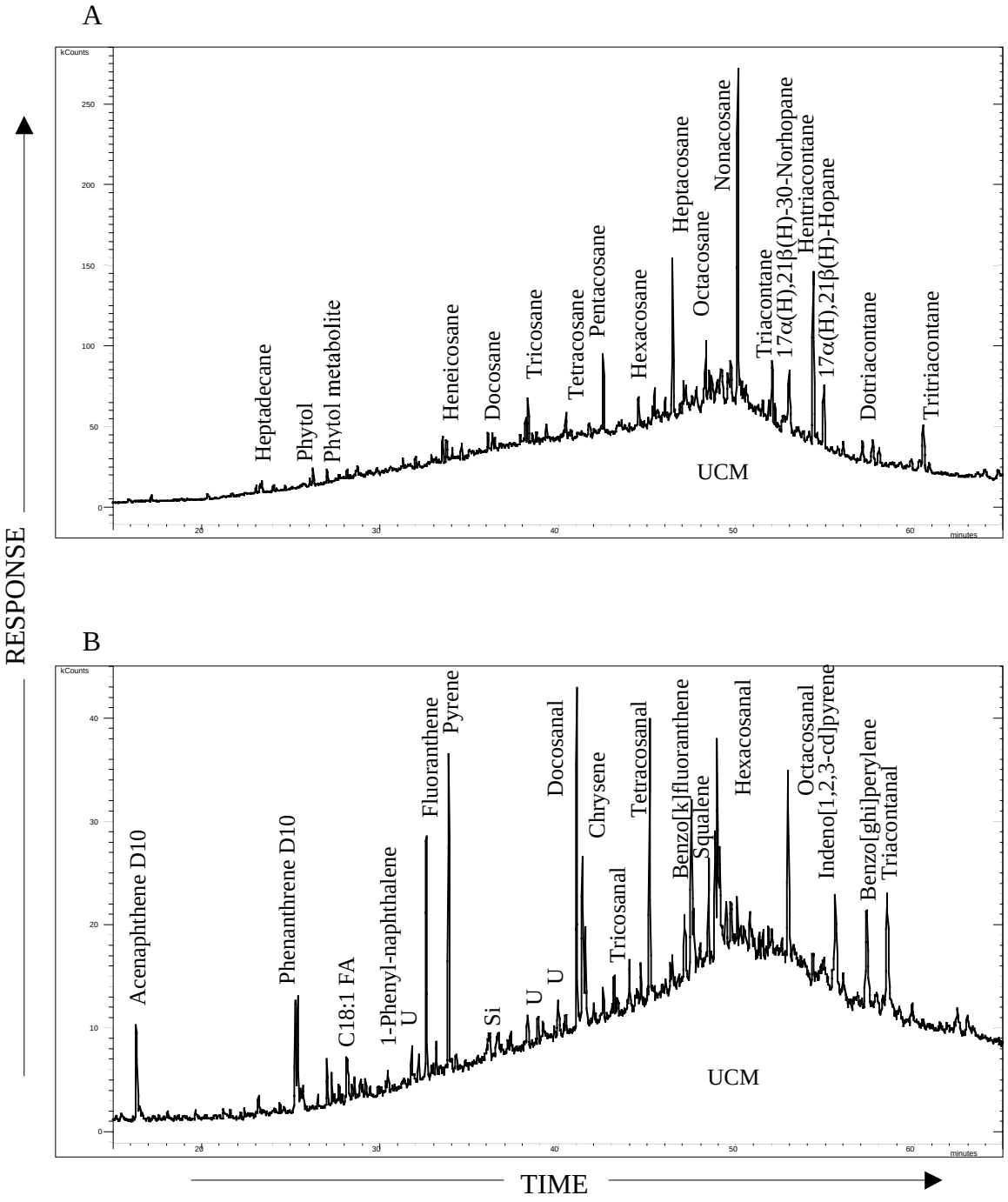
Appendix 23. GC-MS total ion current traces of a 1994 river water sample from San Joaquin River, Manteca, showing dissolved organic components: A) fraction 1, and B) fraction 2 expanded. Abbreviations: BDE = bromo diphenyl ether, BHT = butylated hydroxytoluene, Si = silicone, U = unknown.



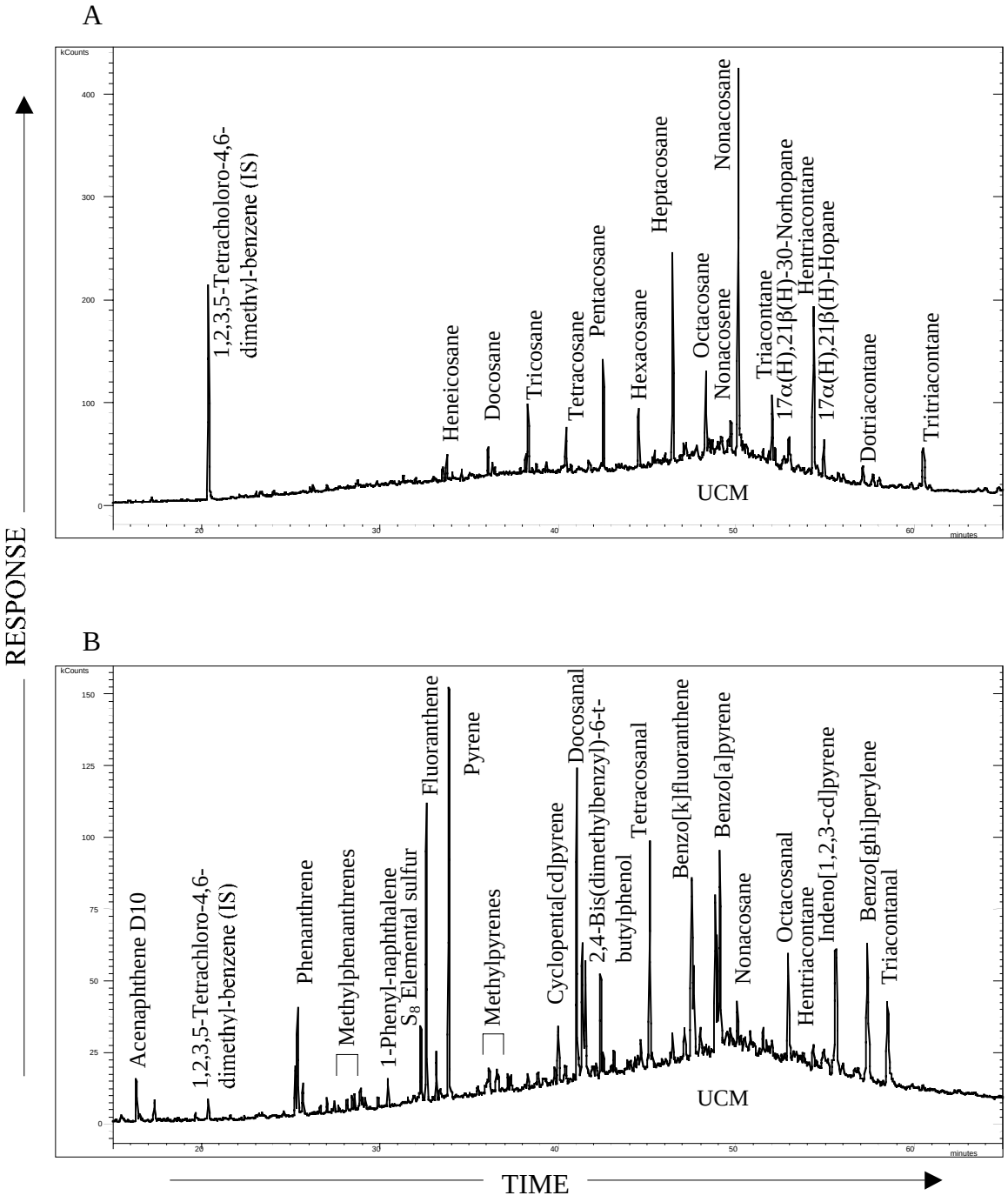
Appendix 24. GC-MS total ion current traces of a 1994 river water sample from San Joaquin River, Manteca, particulate organic components: A) fraction 1, and B) fraction 2. Abbreviations: BDE = bromo diphenyl ether, BHT = butylated hydroxytoluene, FA = fatty acid, Si = silicone, U = unknown.



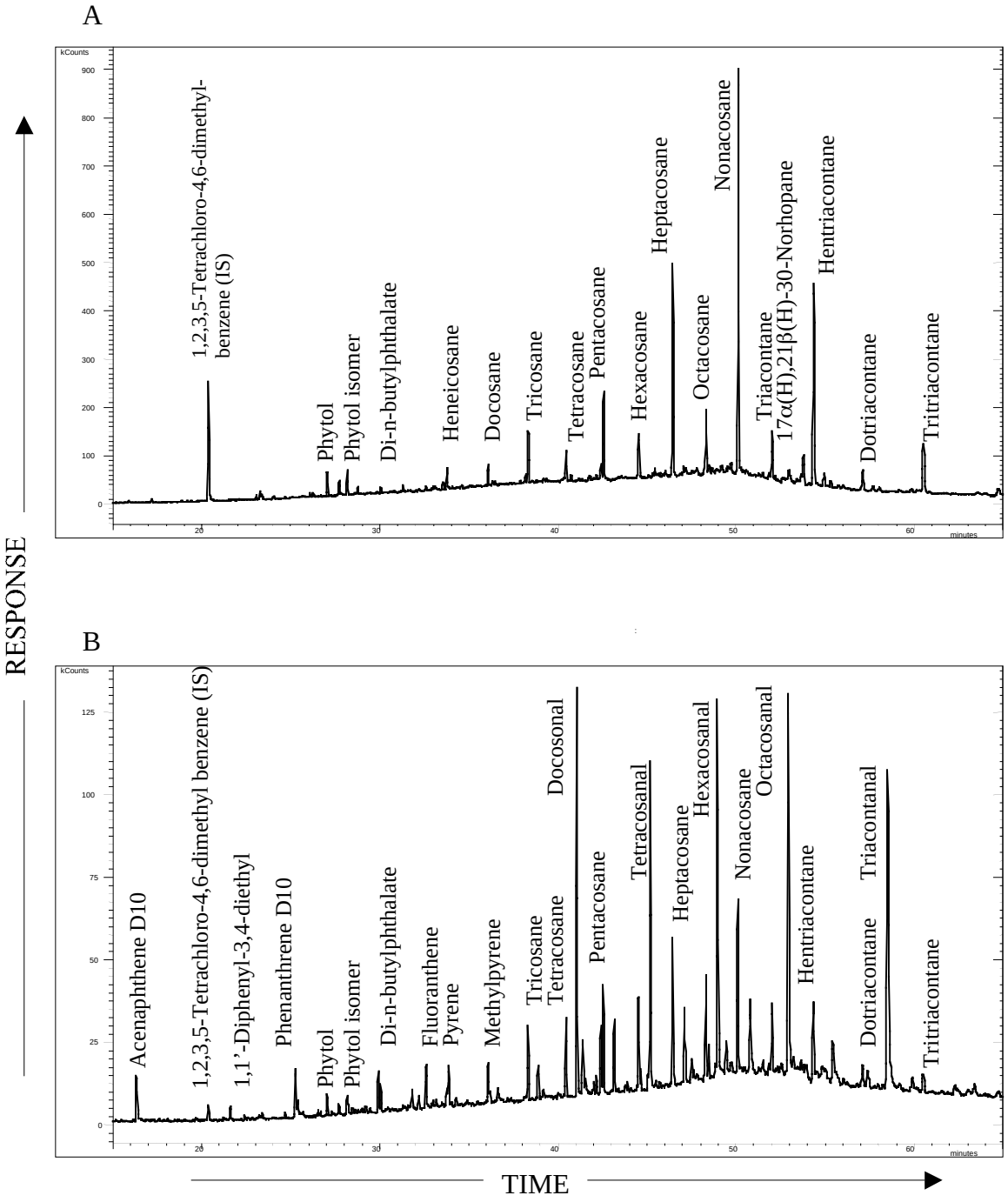
Appendix 25. GC-MS total ion current traces of a 1993 sediment sample from Dumbarton Bridge showing organic components: A) fraction 1, and B) fraction 2. Abbreviations: IS = internal standard, U = unknown, UCM = unresolved complex mixture.



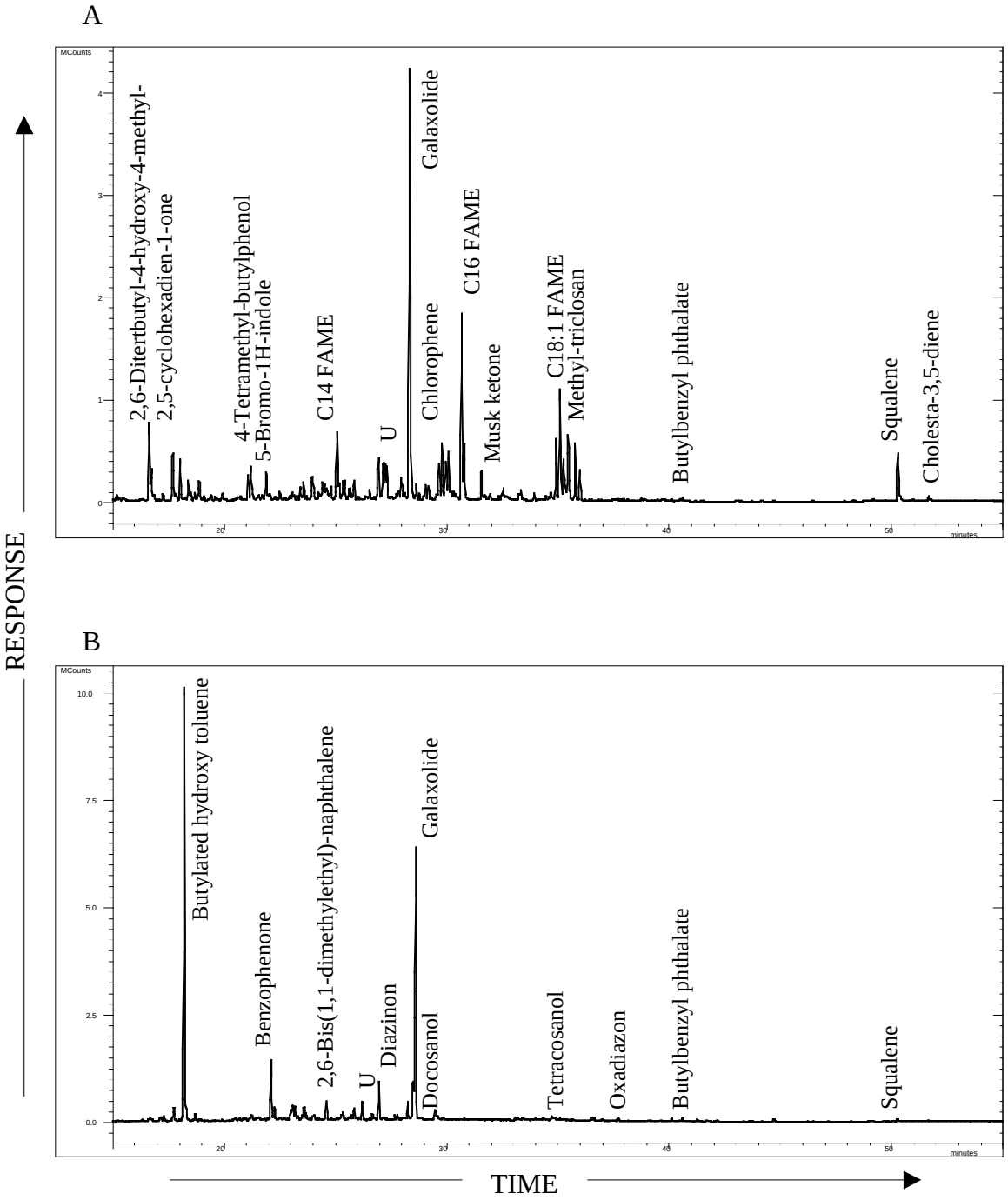
Appendix 26. GC-MS total ion current traces of a 1993 sediment sample from Yerba Buena Island showing organic components: A) fraction 1, and B) fraction 2. Abbreviations: FA = fatty acid, Si = silicone, U = unknown, UCM = unresolved complex mixture.



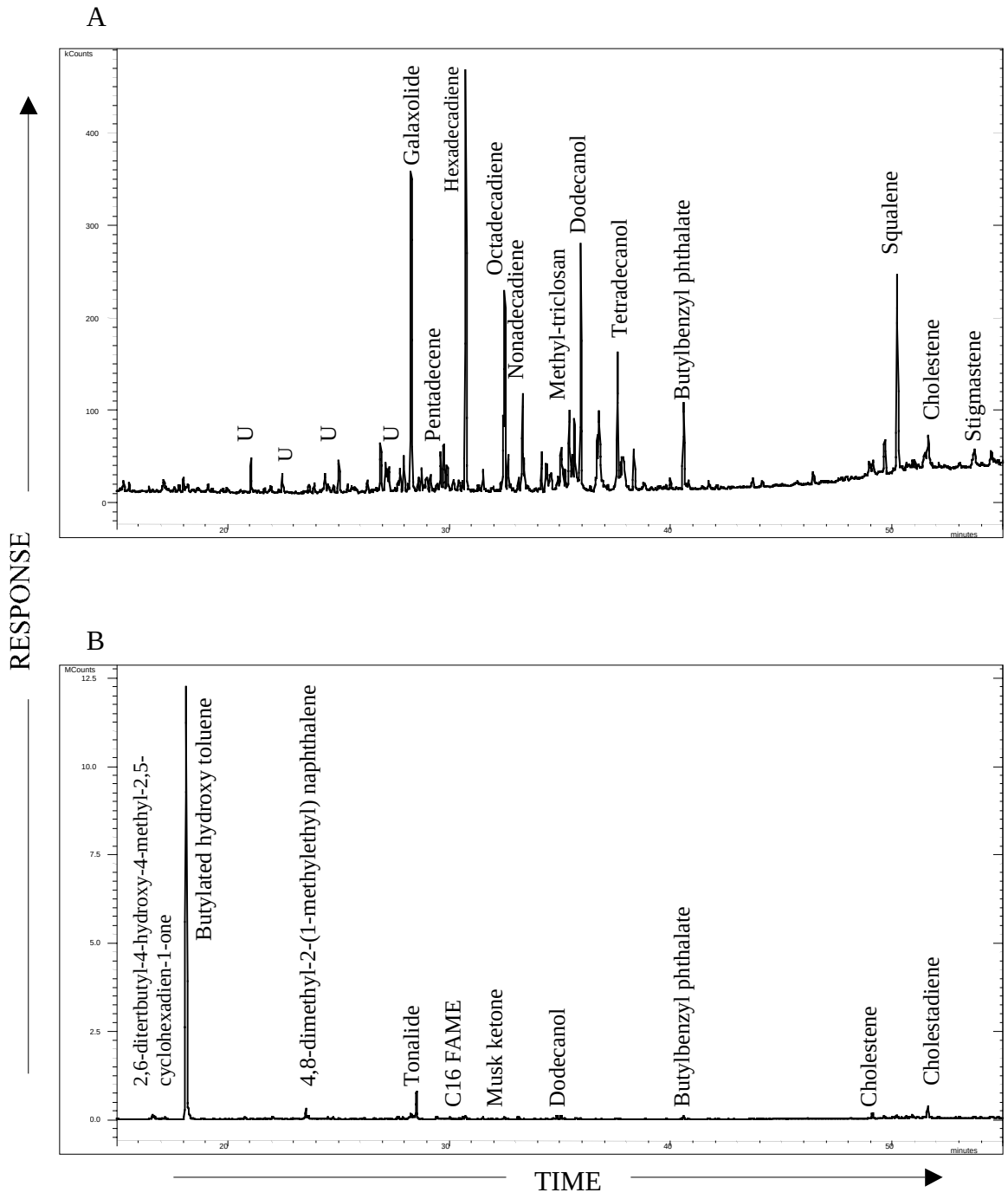
Appendix 27. GC-MS total ion current traces of a 1993 sediment sample from San Pablo Bay showing organic components: A) fraction 1, and B) fraction 2. Abbreviations: IS = internal standard, U = unknown, UCM = unresolved complex mixture.



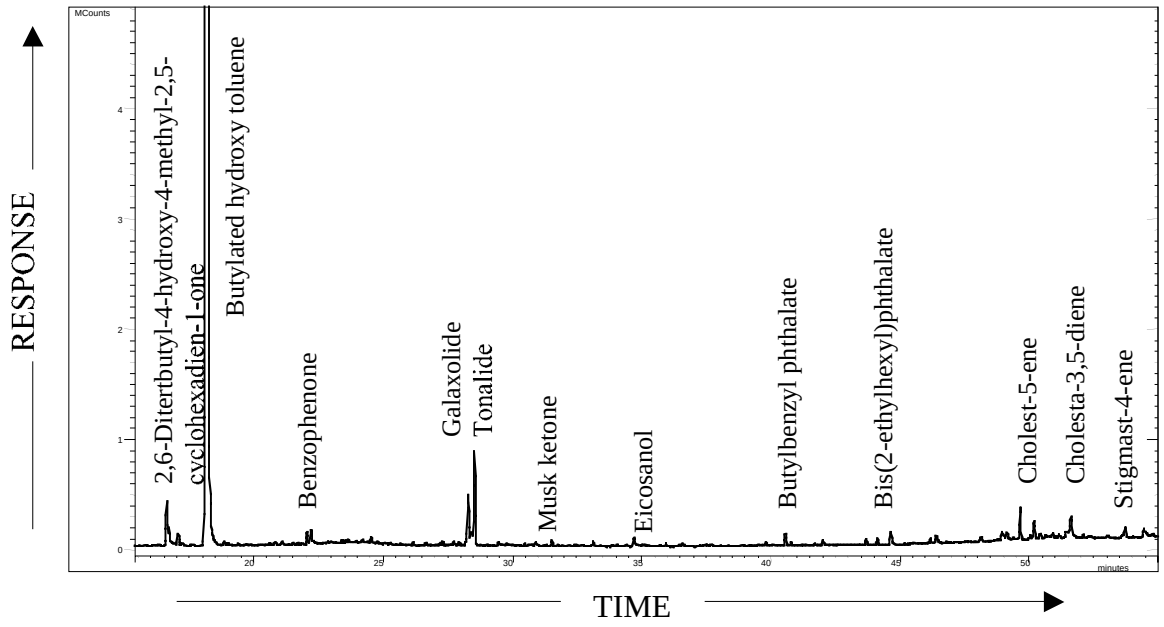
Appendix 28. GC-MS total ion current traces of a 1993 sediment sample from Grizzly Bay showing organic components: A) fraction 1, and B) fraction 2. Abbreviation: IS = internal standard.



Appendix 29. GC-MS total ion current traces of a 1998 Palo Alto treated wastewater final effluent dissolved sample: A) fraction 2, and B) fraction 3. Abbreviations: FAME = fatty acid methyl ester, U = unknown.



Appendix 30. GC-MS total ion current traces of a 1998 Palo Alto treated wastewater final effluent particulate sample: A) fraction 2, and B) fraction 3. Abbreviations: FAME = fatty acid methyl ester, U = unknown.



Appendix 31. Expanded GC-MS total ion current trace of a 1998 Palo Alto treated wastewater final effluent sample composite of F2 and F3 fractions.

Appendix 32. Compounds recommended for addition to the 2002 RMP trace organics analyte lists for water, sediment, and bivalve tissues.

Polybrominated Diphenyl Ethers (Water, Sediment and Tissues)

BDE-17	2,2',4-triBDE
BDE-28	2,4,4'-triBDE
BDE-47	2,2',4,4'-tetraBDE
BDE-66	2,3',4,4'-tetraBDE
BDE-82	2,2',3,3',4-pentaBDE
BDE-85	2,2',3,4,4'-pentaBDE
BDE-99	2,2',4,4'5-pentaBDE
BDE-100	2,2',4,4',6-pentaBDE
BDE-128	2,2',3,3',4,4'-hexaBDE
BDE-138	2,2',3,4,4',5'-hexaBDE
BDE-153	2,2',4,4',5,5'-hexaBDE
BDE-154	2,2',4,4',5,6'-hexaBDE
BDE-183	2,2',3,4,4',5',6-heptaBDE
BDE-190	2,3,3',4,4',5,6-heptaBDE
Octa-BDE	
Nona-BDE	
BDE-209	2,2',3,3',4,4',5,5',6,6'-decaBDE

Nitro and Polycyclic Musks (Bivalve tissue only)

Musk ambrette
Musk ketone
Musk xylene
Celestolide™
Galaxolide™
Tonalide™
Versalide™

Phthalates (Water, Sediment and Tissues)

Bis(2-ethylhexyl)phthalate
Butylbenzyl phthalate
Di-n-butylphthalate

Others (Water, Sediment and Tissues)

p-Nonylphenol
Triphenylphosphate