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Highlights

- Vertical transport and lateral transport across the continental margin were the dominant processes driving seasonal input of particulate matter
- *n*-alkane and sterol biomarker results combined with isotopes and trace metals, offers a multi dimensional approach for deciphering organic matter sources
- Elevated Chlorophyll-*a* and sterol concentrations and contemporaneous increase in the particle reactive micronutrients during the spring sampling period capture seasonal influx of relatively fresh phytodetritus.
- Connectivity to adjacent watershed facilitates offshore transport of "aged" terrestrial organic matter and nutrients

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24 Abstract

25 Submarine canyons are often hotspots of biomass due to enhanced productivity and funneling of 26 organic matter of marine and terrestrial origin. However, most deep-sea canyons remain poorly studied 27 in terms of their role as conduits of terrestrial and marine particles. A multi-tracer geochemical 28 investigation of particles collected yearlong by a sediment trap in Baltimore Canyon on the US Mid-29 Atlantic Bight (MAB) revealed temporal variability in source, transport, and fate of particulate matter. Both organic biomarker composition (sterol and *n*-alkanes) and bulk characteristics ($\delta^{13}C$, $\Delta^{14}C$, Chl-*a*) 30 31 suggest that while on average the annual contribution of terrestrial and marine organic matter sources 32 are similar, 42% and 52% respectively, marine sources dominate. Elevated Chlorophyll-a and sterol 33 concentrations during the spring sampling period highlight a seasonal influx of relatively fresh 34 phytodetritus. In addition, the contemporaneous increase in the particle reactive micronutrients 35 cadmium (Cd) and molybdenum (Mo) in the spring suggest increased scavenging, aggregation, and sinking of phytodetrital biomass in response to enhanced surface production within the nutricline. 36 37 While tidally driven currents within the canyon resuspend sediment between 200 and 600 m, resulting 38 in the formation of a nepheloid layer rich in lithogenic material, near-bed sediment remobilization in 39 the canyon depositional zone was minimal. Instead, vertical transport and lateral transport across the

40 continental margin were the dominant processes driving seasonal input of particulate matter. In turn,
41 seasonal variability in deposited particulate organic matter is likely linked to benthic faunal
42 composition and ecosystem scale carbon cycling.

43

44 Keywords

Submarine canyons; deep-sea ecosystems; sediment trap; geochemical analyses; organic matter
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1. Introduction

49 Submarine canyons play a key role in modulating the flux of particulate organic and inorganic matter 50 to the deep ocean, particularly given that continental shelves and slopes are productive and dynamic 51 ocean margin systems. As a result, canyons are often conduits for the transport of sediments, organic 52 matter, and contaminants from continental margins to the abyssal plain, providing effective 53 connections between highly productive shelf waters and the food limited deep-sea (Canals et al., 2006; 54 Palanques et al., 2006; Costa et al., 2011; Levin and Sibuet, 2012; Puig et al., 2012). Contemporary 55 sedimentary processes within canyons include storm induced turbidity currents, advection through 56 shelf resuspension, slope failures, internal waves, trawling, and dense shelf cascading (see review by 57 Puig et al., 2014). Through the channeling and concentrating of organic matter via dynamic physical 58 processes, canyon fauna can experience enhanced food supply (Vetter and Dayton, 1998; Duineveld et 59 al., 2001; De Leo et al., 2010). Therefore, submarine canyons can potentially be hotspots of 60 biodiversity where enhanced fluxes of organic matter and deposition sustain tremendous benthic 61 biomass in the deep sea compared with nearby open slope habitats at similar depths (Levin *et al.*, 2001; 62 Garcia et al., 2007; De Leo et al., 2010). Within canyons, different physical regimes can substantially 63 alter the organic composition of sediments and the abundance of fauna thriving on these resources. For 64 example, local deposition centers of sediment and organics are hotspots of detritivorous bottom 65 dwelling organisms in the Portuguese Nazaré and New Zealand's Kaikoura canyons (De Leo et al., 66 2010). Furthermore, episodic events known to affect benthic biomass and biodiversity, such as 67 sediment cascades enriched in organic matter (Canals et al., 2006), or increased seasonal productivity 68 in surface waters due to upwelling along canyon edges (Soltwedel, 2000; Garcia et al., 2007; Howatt 69 and Allen, 2013), can temporarily trigger increased sedimentation and/or food availability.

70

Submarine canyons are a major feature incising the United States Atlantic continental margin, from Cape Hatteras to Atlantic Canada. In this region, canyons act as conduits and reservoirs of shelfsourced sediments, transporting this material from the shelf to the slope. The MAB shelf within or near

74 canyons is known for high organic inputs resulting from enhanced surface water productivity (Schaff 75 et al., 1992; DeMaster et al., 1994; Rex and Etter, 2010). This region also contains a high diversity of unique habitats within a relatively small area, some recognized as rich coral habitats and important 76 77 areas for the diversity of the MAB (Hecker, 1980; Hecker et al., 1983). The MAB is incised by 13 major canvons of varying size, shape, and morphological complexity (Obelcz et al., 2014). Baltimore 78 79 Canyon represents one of the best studied canyons in this region (e.g., Gardner, 1989a, b) and was the 80 focus of a multi-year study to better understand the unique hard bottom and soft-sediment communities 81 within and adjacent to the canyon (Brooke and Ross, 2014; Brooke et al., 2016). Recent results from 82 Baltimore Canyon have identified discrete resuspension and deposition zones in the upper canyon and 83 the deeper part of the canyon, respectively. Differences in benthic infaunal communities of Baltimore 84 Canyon appear to be linked to this zonation, as previously documented in other canyon and margin 85 settings where benthic community patterns vary with depth and organic matter (OM) content (e.g., (Carney et al., 2005; Gibson et al., 2005; Wei et al., 2010). For example, in Baltimore Canyon reduced 86 87 infaunal diversity and enhanced infaunal density observed at 900 m was coincident with a zone of 88 organically enriched, finer sediments, characterizing the depositional zone (840 to 1180 m) of the 89 lower reaches of the canyon. In addition to spatial patterns of sediment deposition and organic 90 composition, temporal variations in the transport of both marine and terrestrial organic matter can 91 impact benthic community composition and trophic status (Pusceddu et al., 2009), as well as the deep-92 sea carbon cycle through changes in ingestion, assimilation, and respiration (e.g., Vetter and Dayton, 93 1998; Hunter et al., 2013). For example, Hunter et al. (2013) observed changes in macrofaunal feeding 94 activity and bacterial C uptake as a result of changes in particulate organic matter (POM) composition. 95 Therefore seasonal variations in organic matter flux are key factors influencing deep-sea ecosystems 96 (Gooday, 2002).

97

98 A major aim of this study is to better understand the provenance signature of particle (food) delivery 99 within a submarine canyon by analyzing a suite of geochemical tracers (e.g., stable and radio-isotopes, 100 lipid biomarkers, ²¹⁰Pb, trace metals) collected during a 1-year sediment trap deployment and CTD 101 profiling. While an arsenal of biomarker compounds (e.g., *n*-alkanes, sterols, fatty alcohols, fatty acids, 102 lignin phenols) exist to identify biotic sources as well as yield information on decomposition and 103 diagenesis (e.g., Bianchi and Canuel, 2011 and references therein), ambiguities do exist when 104 elucidating sources of organic matter based on biomarker composition given overlapping sources (e.g., 105 Volkman et al., 2008). Therefore, combining the n-alkane and sterol biomarker results with the other 106 tracers (i.e., stable isotopes, trace metals, radiocarbon) presented here offers a multi dimensional

approach for deciphering organic matter sources (e.g., Wakeham and McNichol, 2014). By building
on previous research demonstrating the utility of hydrocarbons as tracers of organic matter source in
the aquatic ecosystem (e.g., Volkman, 1986; Meyers, 1994; Goni *et al.*, 1997; Wakeham *et al.*, 1997;
Eglinton and Eglinton, 2008; Wakeham and McNichol, 2014), we can investigate the primary sources
of organic matter within Baltimore Canyon. Taken together this detailed study highlights for the first
time key observations describing the temporal variability of organic matter flux that influences the
deep-sea ecosystems within Baltimore Canyon

- 114
- 115 **2.** Materials and Methods

116 2.1 Study Area: Baltimore Canyon

117 Baltimore Canyon, a shelf-sourced canyon is located approximately 125 km southeast of the entrance 118 to Delaware Bay, extends for a distance of 25 km until it merges onto the abyssal plain at a depth of 119 1500 m (Fig. 1). Near the head of the canyon, the width is 3 km and increases to 8 km at the shelf 120 break at a depth of 100 m. Several meanders characterize the canyon, with the canyon axis curving 121 southward at the upper reaches and then turning eastward with increasing depth until it is oriented east-122 west at 3000 m water depth (Obelcz et al., 2014) (Fig. 1). A series of bathymetric steps and terraces 123 are found near the head of the canvon where the cross-sectional profile is V-shaped and transitions into 124 a U-shaped canyon at 1000 m (Obelcz et al., 2014).

125

126 Sediment supply to Baltimore Canyon is from the pelagic zone and reworked shelf sediment (Gardner, 127 1989b) mainly transported via off-shelf spill in canyon heads, failure of the steep canyon walls, and 128 resuspension by bottom currents and internal waves (Obelcz et al., 2014), as well as small-scale mass 129 wasting events triggered by bioerosion (Valentine et al., 1980). Within the canyon, currents focused by 130 the canyon axis in the form of tidal bores and internal waves resuspend sediment between 131 200 and 600 m and sometimes down to 800 m allowing these sediments to be transported down canyon 132 along density surfaces (Gardner, 1989a, b). Resuspension occurs primarily during flood and to a lesser 133 extent during ebb flows and is most intense and episodic when the water is poorly stratified 134 (i.e., during late winter and early spring), though episodic events may occur at other times of the year 135 (Gardner, 1989a, b).

136

137 2.2 Sediment Traps

Two benthic landers, each consisting of an aluminum tripod frame approximately 2 m in height equipped with twin acoustic releases and eight buoyancy spheres were deployed on September 5, 2012

140 at a depth of 603 m (38° 09.024 N, 73° 50.954 W, described as the shallow lander) and at 1318 m (38° 141 02.543 N, 73° 44.153 W, described as the deep lander) (Fig. 1). Each lander was equipped with a 142 Technicap PPS 4/3 sediment trap programmed to rotate a 250 mL sample bottle at either 20 or 30-day 143 intervals, delivering 12 samples during the 1-year deployment. Temperature, salinity, turbidity, 144 dissolved oxygen, and bottom currents were measured using an Aanderaa (RCM) string logger. All 145 RCM probes were mounted approximately 1.5 m off bottom with the exception of the current meter, 146 which was approximately 2 m off the bottom. In addition, a mooring was deployed August 18, 2012 at 147 1082 m (38° 04.657 N, 73° 46.957 W, described as the mid-mooring) (Fig. 1). The mooring was equipped with a Honjo Parflux sediment trap with thirteen 500 mL bottles mounted 4 m above bottom 148 149 programmed to rotate on a 30-day interval. The sampling design enabled the examination of canyon 150 characteristics, including the movement of particulate material up and down canyon, propagation of 151 internal waves, water parameter variability, and particle fluxes.

152

153 Biological activity in the sediment traps was inhibited by treating the traps with a pH buffered solution 154 of mercuric chloride (HgCl₂) in seawater, which has been shown to be an effective means to limit 155 microbial activity and subsequent alteration of organic matter (e.g., Lee et al., 1992). While not 156 immune to diagenesis/degradation within the water column (e.g., Wakeham et al., 1997; Tolosa et al., 157 2003), the retention of a "biological heritage" of lipid extraction (e.g., *n*-alkanes and sterols) from 158 sediments is less sensitive to alteration and degradation and represents important organic geochemical 159 proxies that are preferentially preserved relative to other classes of biomarkers (see reviews by 160 Volkman, 1986; Meyers, 1994; Eglinton and Eglinton, 2008). Early on Prahl et al. (1980) 161 demonstrated a decrease in aliphatic hydrocarbon distribution in surface sediments relative to trap 162 sediment. Similarly, previous work has demonstrated the preferential removal of labile components 163 and enrichment of residual recalcitrant matter in surface sediment relative to trap material (e.g., 164 Wakeham and Canuel, 2006; Wakeham and McNichol, 2014).

165

The complete time-series from the shallow (603 m) and mid-depth (1082 m) trap sites were compromised by mass flux events (in October 2012) that filled the trap funnels completely, leaving only a few samples intact. The flux estimate may be unreliable since the elevated current speeds surpass the settling velocity of particles (Knauer and Asper, 1989). The only sediment trap with an almost complete sampling series was retrieved from the deepest Baltimore Canyon lander site (1318 m). The missing dates represent sediment trap bottles that were partially open upon retrieval, therefore precluding accurate flux measurements and sample preservation. Sediment trap samples were split 173 into five equal splits with a rotor splitter at the Royal Netherlands Institute for Sea Research (NIOZ). 174 Two splits were rinsed thoroughly to remove sea salt and HgCl₂, after which they were frozen, freeze 175 dried, and weighed to calculate mass fluxes and prepared for geochemical analyses. To keep samples 176 intact for pigment analysis, another split was rinsed with filtered seawater from the deployment site 177 after which it was freeze dried.

178

179 2.3 Water column properties

180 Vertical profiles were made of the water column properties using a CTD-rosette (SBE 911plus CTD 181 profiler and a rosette containing twelve 5 L Niskin bottles) deployed inside Baltimore Canyon to 182 establish if the canyon acts as conduit for suspended and dissolved material. One CTD transect was 183 taken down the axis of the canyon, and during these casts, the CTD array was lowered from the surface 184 to as close to the bottom as feasible (usually about 10 m above bottom) (Fig. 1). Seawater samples 185 were collected during the upcast of the CTD at shallow (250 m), mid (644 m), and deep (1140 m) sites 186 within Baltimore Canyon, as well as at mid-depth shelf sites (678 m) outside the canyon for 187 measurements of nutrient concentrations, trace metals, and POM (>0.45 µm). Seawater was filtered 188 directly from the Niskin bottles using acid-cleaned Teflon coated tubing attached to a polypropylene 189 filter holder that was preloaded with an acid-cleaned polysulfone filter and attached to a vacuum pump. 190 Filters were pre-cleaned by soaking in trace metal grade HCl in a 1 L low-density polyethylene bottle. 191 Replicate water samples were collected from two 5 L Niskin bottles at each sampling depth. Water 192 column particulate matter for trace element measurements was collected by filtering approximately 5 L 193 of seawater on acid-cleaned 0.45 µm polysulfone filters (47 mm) given low blank concentrations 194 (Planquette and Sherrell, 2012). The filter holders with preloaded filters were double bagged in 195 polyethylene zip-lock bags and kept frozen for transport back to the laboratory.

196

197 Seawater samples collected for dissolved nutrient analysis were stored in acid-cleaned high-density 198 polyethylene 20 mL scintillation vials, which were triple washed with extra filtrate before saving the 199 final sample for analysis. These samples were frozen immediately until analyzed at the Geochemical 200 and Environmental Research Group at Texas A&M University, College Station. Nutrient samples were 201 analyzed on an Astoria-Pacific auto-analyzer. The nitrate/nitrite/silicate methods are based on 202 Armstrong et al. (1967). Phosphate methods are based on Bernhardt and Wilhelms (1967). Ammonium 203 methods are based on Harwood and Kühn, (1970). The dissolved inorganic nitrogen (DIN) 204 concentrations were calculated as the sum of nitrite, nitrate, and ammonium concentrations. Analytical 205 detection limits were 0.01 μ M for phosphate, 0.003 μ M for nitrite, 0.05 μ M for nitrate and silicate, and 206 0.08 μ M for ammonium.

207

208 2.4 Geochemical Analyses

209 Sediment organic carbon and nitrogen content were measured on a Thermo Organic Elemental 210 Analyser Flash 2000, and stable carbon and nitrogen isotopes were measured on a Thermo Delta V Advantage Isotope Ratio MS at NIOZ. Prior to analysis, samples for C_{org} and $\delta^{13}C$ analysis were 211 acidified with HCl to remove all inorganic carbon. Standards used for C were acetanilide and benzoic 212 213 acid, respectively (analytical detection limits $\delta^{13}C = 0.3\%$). Samples for %N and $\delta^{15}N$ analysis were 214 not acidified and standards used were acetanilide and urea respectively (analytical detection limits δ^{15} N 215 =0.1‰). Trace element concentrations of the suspended particulate matter and sediment trap material 216 were determined by ICP-MS at the USGS Mass Spectrometry Facilities in Denver, Colorado. Filters 217 were digested following procedures outlined in Planquette and Sherrell (2012). Data presented here 218 were reported in µg g⁻¹ following blank correction, as determined from digesting procedural filter 219 blanks, and sample and filter weight corrections (Prouty et al., 2016). For the sediment traps, 50 to 220 100 mg of sediment was digested using a 4-acid procedure (HF + HCl + HNO₃ + HClO₄), taken to 221 dryness, and the residue dissolved in 5 to 20 mL of 5% to 13% HNO₃ with a dilution factor of 10³ to 222 10⁴ (Briggs and Meier, 2002).

223

224 Concentrations of chlorophyll *a* and its derivatives (phaeophorbides, phaeophytines) were determined 225 with reverse-phase HPLC according to the method outlined by Witbaard et al., (2000). Phytopigments 226 were identified and quantified using a library based on pigment standards (DHI, Denmark). From the 227 results of the pigment analysis, intact chlorophyll-a concentrations were taken as a proxy for fresh 228 phytodetritus biomass. The chlorophyll-a/phaeopigment ratio was used to indicate the freshness of the 229 trapped phytodetritus. The activity of ²¹⁰Pb was determined by alpha spectrometry from ²¹⁰Po using a 230 Canberra alpha detector, which was extracted from the sample by leaching with concentrated HCl 231 (Boer et al., 2006). The ²¹⁰Pb activity of sediment trap samples was used as an indicator for the relative 232 proportion of suspended and freshly settled material. Fresh settled material has a high ²¹⁰Pb signal, 233 while resuspended material shows lower values due to radioactive decay.

234

Sediment radiocarbon (¹⁴C) ages were determined at the National Ocean Sciences Accelerator Mass
 Spectrometry (NOSAMS) facility, Woods Hole, MA USA. Approximately 50 mg of acidified (1.2N
 HCl) bulk sediment was converted to CO₂ and graphitized for accelerator mass spectrometry (AMS)

(Vogel *et al.*, 1987). Radiocarbon ages were calculated using the Libby half-life of 5568 years. The D¹⁴C values (i.e., radiocarbon values without age correction) were age corrected to account for decay that took place between collection (or death) and the time of measurement using the following equation: $\Delta^{14}C = (Fm*age correction)-1)*1000$ where age correction is defined as exp((1950-year of measurement)/8267), and Fm is fraction modern (Stuiver and Polach, 1977). Radiocarbon results are reported as $\Delta^{14}C$ (‰) and conventional radiocarbon age after applying a measured $\delta^{13}C$ correction (Stuiver and Polach, 1977).

245

246 Molecular composition of the sediment trap samples was determined by gas chromatography-mass 247 spectrometry (GC-MS) at the USGS Pacific Coastal Marine Science Center's (PCMSC) Organic 248 Geochemistry laboratory in Santa Cruz, California as described in Prouty et al. (2016). Approximately 249 1-2 g of freeze-dried organic matter was extracted by pressurized solvent extraction (ASE, Dionex 250 Corp., CA, USA). Samples were extracted with a hexane: acetone (1:1) solvent mixture followed by a 251 second extraction in dichloromethane:methanol (2:1) solvent mixture. Internal standards (5-a-252 androstane, 5- α -androstan-3- β -ol) were added to samples prior to extraction. All glassware was 253 washed, solvent rinsed (methanol, hexane, and dichloromethane), and combusted at 400°C overnight. 254 Blanks were run for the entire procedure, including extraction, solvent concentration, and purification. After evaporation of extracts to 5 ml volume utilizing TurboVap Evaporation Concentrator (Zymark 255 256 Corp., NC,USA), samples were loaded onto liquid chromatography columns for compound class 257 separation. Each column was layered with 2.5 g of 5% deactivated alumina, 2.5 g of 62 silica gel and 258 5.0 g of 923 silica gel, which had previously been activated at 500° C for 8 h and then, in the case of 259 the alumina, partially deactivated with ultrapure water (5% w/w). Three separate fractions were 260 collected: F1-saturate (100% hexane eluent); F2-aromatic (30% DCM : 70% hexane eluent); and, F3-261 polar (50% ethyl acetate: 50% hexane) and reduced in volume to 1.0 ml. The polar fraction (F3) was 262 further derivatized with BSTFA (N,O-bis(trimethylsilyl) trifluoroacetamide) containing 2% TMCS 263 (trimethylchlorosilane) and anhydrous acetonitrile. Extracts were analyzed by splitless injection onto 264 an Agilent 6890 gas chromatograph interfaced to an HP 5973 mass spectrometer (GC-MS) at the 265 USGS PCMSC Organic Geochemistry Laboratories in Santa Cruz, CA. The gas chromatograph oven 266 program had an initial temperature of 90°C which was held for 4.0 min then ramped at 5°C min⁻¹ to a 267 final temperature of 310°C which was held at this final temperature for 10 min. The capillary column 268 (DB-5MS: 30 m length, 0.25 mm id with a 25 µm phase thickness) was directly interfaced to the ion 269 source of the mass spectrometer. Hexane instrument blanks and procedural sample duplicates were 270 run and analyzed for every 10 samples. Compound identifications were made by comparison with

known analytical standards and/or published reference spectra (Fig. S1). Concentrations of individual lipids are blank corrected values. Lipid biomarkers (sterol and *n*-alkane) concentrations (μ g g⁻¹) are reported normalized to organic carbon of dry sediment as measured by a coulometer at the PCMSC.

274

275 Major organic matter sources to the sterol and *n*-alkane molecular signatures were investigated by 276 calculating relative proportions of marine, terrestrial, and anthropogenic/petroleum contributions. 277 Relative contributions from natural (marine versus terrestrial) and anthropogenic organic matter *n*-278 alkane and sterol sources were calculated following a modified designation from Pisani et al. (2013). 279 Terrestrial organic matter composition of sediments was quantified using concentrations of 280 odd-numbered *n*-alkanes in the C_{21} to C_{31} range as well as the sterols campesterol, stigmasterol, β-sitosterol and stigmastanol (the reduced from of stigmasterol). Marine components were determined 281 282 using concentrations of the sterols cholesterol, 22-dehydrocholesterol, brassicasterol, and cholestanol 283 (reduced form of cholesterol) as well as odd- and even-numbered *n*-alkanes in the C_{15} to C_{19} range. 284 The anthropogenic components were determined using the sterol composition of coprostanol, 285 epicoprostanol, and the ketone, $5-\beta$ -coprostanone, in addition to the isoprenoid hydrocarbons pristane 286 and phytane.

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- 288 289

3. Results and Discussion

290 *3.1 Environmental and Water Column Variability*

291 The three benthic observatories positioned throughout the canyon recorded decreases in current speed, 292 turbidity, and temperature with depth (Fig. 2). The shallow lander (603 m) was positioned in the most dynamic area of the canyon, with temperatures fluctuating between 4.5- 8.6 °C and a mean of 5.4 °C 293 294 (standard deviation [SD] 0.47 °C). The intensity of the current also varied greatly, with peak current velocity reaching 66.2 cm s⁻¹ and a mean of 13.7 cm s⁻¹ (SD 9.03 cm s⁻¹). Peaks in turbidity appeared 295 296 to correspond with temperature fluctuations (Spearman's Rank Correlation on 24 hour moving average 297 data for first deployment, r = 0.48, p < 0.001). In contrast, the mid-mooring area (1082 m) was cooler (temperatures between 4 °C-5.1° C and a mean of 4.5 °C [SD 0.16 °C]) and had a lower current 298 299 velocity (maximum current velocity: 42.3 cm s⁻¹, and mean: 8.7 cm s⁻¹ [SD 5.6 cm s⁻¹]). Current 300 velocity and temperature were positively correlated at the mid-mooring location (Spearman's Rank Correlation on 24 hour moving average data for first deployment, r = 0.43, p < 0.001). The deeper 301 302 region of Baltimore Canyon (1318 m) was cooler and had lower current velocities (temperatures 303 between 3.8-4.74 °C with a mean of 4.2 °C [SD 0.16 °C]) relative to the shallower deployments. 304 Maximum current velocity was 29.2 cm s⁻¹, with a mean speed of 6.6 cm s⁻¹ [SD 3.27 cm s⁻¹]. At the

305 deep site, peaks in turbidity were positively correlated with current velocity (Spearman's Rank 306 Correlation on 24 hour moving average data for first deployment, r = 0.62, p < 0.001), and there was a 307 strong positive relationship between current velocity and temperature (Spearman's Rank Correlation on 24 hour moving average data for first deployment, r = 0.75, p < 0.001), consistent with the patterns 308 309 recorded by the shallow and mid-canyon instruments. All sites indicated that warmer, sediment-laden 310 waters are transported to the deeper parts of the canyon during part of the tidal cycle. Current driven 311 bed shear stress (>0.1 N m⁻²) was calculated from the sediment density and grain size, as well as the 312 kinematic viscosity and density of the seawater. Based on this calculation, sediment remobilization 313 varied throughout the canyon, with current driven bed shear stress sufficient to resuspend fine-grained 314 material (i.e. <34 µm) 15% of the time at the shallow area of the canyon, but only 1% at the mid 315 canyon and less than 0.02% in the deeper area. Plots of progressive current vectors demonstrated a 316 strong tidal flow at the shallow lander station, with a general movement towards the northeast, up 317 canyon. However, some disruption to this pattern was observed during certain periods throughout the 318 year when flow moved down canyon (Fig. 1). The canyon walls steered water movement within the 319 mid-canyon station, but disruption to the general up-canyon movement was detected during September 320 to November and January to March (Fig. 1b). During the periods of October to November 2012 and 321 March to May 2013, turbidity events in the shallow lander site were followed by a 2 °C temperature 322 increase, and accentuated by elevated current speeds and flow to the north (Fig. S2), suggesting a 323 possible link to benthic storms associated with Gulf Stream meanders and rings (Gardner *et al.*, 2017). 324 This signal was less distinct in the deeper sites where temperature fluctuations were substantially 325 smaller. The deep lander had the most consistent residual flow that was identical in direction to the 326 shallow station (Fig. 1a and c). However, such transport was less tidally regulated than in the shallow 327 station demonstrating a greater movement to the northeast.

328

329 The CTD transects conducted in Baltimore Canyon reveal a large intermediate nepheloid layer 330 extending from the mouth of the canyon from 200 m to approximately 900 m (Fig. 3), with enhanced 331 turbidity during both up and down canyon flow. This nepheloid layer was also observed by Gardner, 332 (1989a, b), and likely forms a permanent feature in Baltimore Canyon in response to internal wave 333 energy at tidal frequencies. The nepheloid layer, between 400 and 800 m, and a second, smaller patch 334 in the surface water near the canyon wall (8 km down canyon) (Fig. 3), was characterized by increased 335 lithogenic material, specifically aluminum (Al), neodymium (Nd), Iron, (Fe), and lanthanum (La) (Fig. 336 4). Particulate (>0.45 μ m) element concentrations were enriched at the shallow (NF-2012-138; 261 m) 337 and mid-depth (NF-2012-128; 644 m) CTD stations whereas trace element profiles at the deep (NF- 338 2012-130; 1140 m) and slope (NF-2012-149; 668 m) CTD stations did not exhibit elevated trace metal 339 particulate concentrations at 600 m (Fig. 4). Trace element composition for the Baltimore Canyon 340 slope site was consistently low and the deep site only showed a slight enrichment near the bottom (NF-341 2012-130; 1140 m). These results indicate that the nepheloid layer appears restricted to within the 342 canyon and to a depth of 850 m.

343

344 Nutrient profiles in Baltimore Canyon displayed surface-water depletion and bottom-water enrichment 345 in nitrate, phosphate, and dissolved silicate (Fig. 5). These results illustrate the uptake of nutrients 346 within the nutricline due to biological processes, particularly the growth of phytoplankton in the photic 347 zone. The interaction between phytoplankton growth and nutrient uptake is illustrated in the inverse 348 relationship between the nutrient and dissolved oxygen (O_2) profiles (Fig. 5). Below the mixed layer, 349 concentrations of nitrate, phosphate, and dissolved silicate were conservative and exhibited a 350 homogenous distribution at depth. The nutricline in Baltimore Canyon was defined from nutrient 351 profiles collected during the August 2012 sampling cruise. Maximum nutrient concentrations occurred 352 at ~250-300 m, consistent with the thermocline depth in Baltimore Canyon, and agrees with those 353 derived from Ocean Data Viewer (latitude 73° 49.36 N, longitude 38°23.24 W; Schlitzer, 2016). Given 354 the similarity between the individual depth profiles down canyon, the nutricline appears to be 355 homogenous along the length of the canyon with little spatial variability.

356

357 *3.2 Sediment Traps*

358 The sediment trap data at the deep site illustrate a narrow range of mass fluxes during the first seven months (4.7 to 9 g m⁻² d⁻¹) and slightly lower mass flux during the last three months (Fig. 6). There 359 360 were two periods of relatively elevated mass flux, September-October 2012 and January-February 361 2013. The increase in mass flux in September-October 2012 at the deep trap site indicates a 362 resuspension or mass-wasting event, potentially, linked to increase mass fluxes at the shallow and mid-363 depth sites, and subsequent overfilling of the funnels at these shallower depths. Similar sediment trap 364 overfilling was observed in Nazare Canyon, in response to storm-induced turbidity currents (Martín et 365 al., 2011). However, we did not observe overfilling at the deep sediment trap site, suggesting that 366 sediment loading in the shallow and mid-depth regions may not necessarily be transported along the 367 canyon thalweg to the deeper region, and that localized overspill from the canyon walls can help 368 explain asynchronous mass fluxes within the canyon. At the deep trap site, percent C_{org} and total N did 369 not vary significantly between periods and patterns of C and N fluxes and therefore closely resembled 370 those of the mass flux, with a small range in C:N ratios (8.8 to 10.6) (Table 1). ²¹⁰Pb activity at the

deep trap site displayed an inverse temporal pattern relative to mass flux. Higher mass fluxes corresponded to low ²¹⁰Pb values (R=-0.90), indicating trapping of resuspended material (Fig. 6a). Chlorophyll-*a* concentrations showed more variability between successive samples. Peak Chl-*a* flux occurred in May–June 2013, coincident with elevated %C_{org} values and highest Chl-*a* /phaeopigment ratio, indicating a supply of relatively fresh phytodetritus from the spring phytoplankton bloom (see below). A secondary peak in Chl- *a* flux and ²¹⁰Pb was observed in October–November 2012, indicating enhanced transport of phytodetritus (Fig. 6b).

378

379 There was a narrow range in stable carbon (δ^{13} C) and nitrogen (δ^{15} N) isotope values -22.8‰ (SD 0.15) 380 and 4.83‰ (SD 0.23) (Table 1), consistent with a marine signature (Meyers, 1994). The δ^{13} C range 381 was consistent with that reported for POM in the surface and mid-water depths, and $\delta^{15}N$ values were 382 consistent with surface POM values on the Northwest Continental Shelf (Oczkowski *et al.*, 2016). The 383 trap material most likely reflects a combination of freshly exported material and suspended POM. 384 Romero-Romero et al. (2016) were able to use stable isotope signatures to distinguish organic matter 385 sources in the Aviles submarine canyon. However, in our study it was difficult to distinguish between a 386 mixture of marine algae plus terrestrial C3 plants given the narrow range of sediment trap bulk δ^{13} C 387 values (-22.8 to -22.0 ‰). The enriched C:N ratios relative to the Redfield ratio (6.7; Table 1) suggests 388 a mixture of sources of both marine phytodetritus and land-derived organic debris. As shown in Figure 389 7, the sediment trap samples fall along a mixing line between marine algae and C3-vascular plants according to δ^{13} C and C:N values (Goñi *et al.*, 2003; Tesi *et al.*, 2007). 390

391

392 The total concentration of *n*-alkanes for sediment trap samples from the deep lander site represents a 393 resolved *n*-alkane range from C_{14} to C_{32} as well as detectible amounts of the isoprenoid hydrocarbons pristane (pr) and phytane (ph) (Table 2a). Total *n*-alkane concentrations ranged from <1 to $12 \ \mu g \ g^{-1}$ 394 dry weight normalized to organic carbon (µg g⁻¹ C), with September/October 2012 yielding elevated 395 396 *n*-alkane concentrations (Fig. 6b). Overall, the molecular composition was dominated (95%) by higher 397 molecular weight (HMW, $>C_{21}$) *n*-alkanes, particularly *n*-C₂₉ and *n*-C₂₇, except in February 2013 when n-C₂₄ was anomalously elevated (Table 2a) The Carbon Preference Index (CPI) is often used to 398 399 identify organic matter source by describing the molecular distribution of odd number *n*-alkanes 400 relative to even number *n*-alkanes (Bray and Evans, 1961). Overall, there was a strong odd-to-even 401 predominance, with a CPI consistently >1.0, particularly in September/October and June/July (Table 402 2a), suggesting increased OM originating from land plant material (Hedges and Parker, 1976). The 403 dominance of terrestrial plant input relative to aquatic macrophytes is also expressed through the

404 Alkane Proxy (Paq) (Ficken et al., 2000). The Paq values were consistently <1, revealing the 405 dominance of long chain-length n-alkanes. Phytane was detected in the samples from 406 September/October of 2012, but was absent from the other months. The sediment trap sample from 407 May 2013 contained enriched pristane relative to the other months, but overall both pristane and 408 phytane concentrations were $<1 \text{ µg g}^{-1} \text{ C}$ (Table 2a). Total sterol concentrations ranged from 1 to 30 µg 409 g⁻¹ C (Table 2b), and were dominated by cholesterol. In comparison, the smallest contribution was from the anthropogenic-sourced sterols, specifically coprostanol and epicoprostanol. Sterol 410 411 concentrations were elevated in October 2012 when cholesterol contributed 30% of the total sterol 412 concentration. A second peak in sterol concentration occurred in May 2013 and was dominated by both 413 cholesterol and cholestanol, comprising over 60% of the total sterol composition. Both sterols have 414 marine biological sources, such as biosynthesis of plankton organisms and zooplankton (Volkman, 415 1986). The sterol enrichment in the spring is tightly coupled to the peak in Chl-a concentrations (Fig. 416 6b), illustrating the influx of relatively fresh phytodetritus. The influx of fresh phytodetritus is also 417 consistent with the phytoplankton blooms in the spring when net primary productivity exceeded 700 g C m⁻² d⁻¹ (Fig. 6d), as calculated per Behrenfeld and Falkowski (1997) for a 20 km² surrounding 418 419 Baltimore Canyon. In comparison, lower sterol and *n*-alkane concentrations during the winter months 420 reflect a reduction in surface water primary productivity (< 300 g C m⁻² d⁻¹) during the winter season.

421

422 The distribution of biomarkers in the sediment trap organic matter indicates that delivery to the deep 423 area of Baltimore Canyon is a composite of sources (e.g., algal/phytoplankton/zooplankton 424 productivity and land-plant productivity). Anthropogenic sources were minimal, with an annual 425 average contribution of 6%, and the greatest contribution occurring in September 2012. Although high 426 pristane concentrations in sediment can be derived from zooplankton, the pristane/phytane ratios 427 observed in this study are used as indicators of a petrogenic, anthropogenic source (Blumer et al., 428 1963). While on average the contributions from marine (43%) and terrestrial (52%) organic matter 429 sources were similar, seasonal variability in source contribution was observed in the biomarker time 430 series (Table 3). For example, September 2012 and May 2013 were dominated by terrestrial (76%) and 431 marine (71%) sources, respectively. Dominance by terrestrial sources in September 2012 was 432 potentially associated with a resuspension event as captured in the increased mass flux and reduced 433 ²¹⁰Pb values, and potentially linked to enhanced turbidity from overspill of the canyon walls. In 434 contrast, the peak in marine sources in May 2013 is attributed to increased primary production during 435 the spring bloom (Fig. 6d), when freshwater transport is at a maximum during spring discharge (Choi

and Wilkin, 2007), and facilitates offshore transport of both nutrients and terrestrially derived organicmatter.

438

439 A suite of trace elements was measured from the sediment trap samples collected at the deep lander 440 site (Table 4). Iron (Fe) and aluminum (Al) dominated the trace element composition of the sediment 441 traps, but showed little variability throughout the deployment period with average monthly Fe and Al 442 concentrations of 56 and 32 mg g⁻¹, respectively. After Fe and Al, barium (Ba), phosphorous (P), 443 strontium (Sr), and manganese (Mn) contributed to the elemental composition. Variability, evaluated 444 as percent contribution of standard deviation to total elemental concentration, was greatest for 445 cadmium (Cd) and molybdenum (Mo) at 4% and 3%, respectively. Peak values for the particle reactive 446 micronutrients Cd and Mo, occurred in April and May, with a smaller enrichment in October (Fig. 6c). 447 The spring and fall periods are also characterized by enrichment in total sterol concentration as 448 discussed above. During the deployment period, net primary production for the months of April 449 through June 2013 was 721, 698, and 775 g C m⁻² d⁻¹ respectively, whereas net primary production in 450 the fall months of Sept. through Nov. 2012 was 372, 429, and 422 g C m⁻² d⁻¹ respectively (Fig. 6d). 451 Hence, the spring phytoplankton bloom could have fueled the increase and export of fresh organic 452 matter (e.g., phytodetritus) in the canvon during this season. The elevated pigment fluxes correspond to 453 increased biomarker concentrations (especially sterols), indicating greater primary production and 454 export of marine-derived organic matter. The simultaneous increase in the phytoplankton essential 455 micronutrients of Cd and Mo during this period suggests increased scavenging, aggregation, and sinking of biomass during seasonal blooms in response to enhanced surface production within the 456 457 nutricline (Wangersky et al., 1989; Pohl et al., 2004). The synchronous timing of the surface water 458 primary productivity signal relative to the sediment trap geochemistry time series suggests rapid export 459 and sinking of fresh particulate organic matter to the depositional zone of Baltimore Canyon. This corresponds to a spring maximum at the shelf break/slope waters (Ryan et al., 1999; Xu et al., 2011), 460 461 and an increase in biomass on the MAB shelf during the spring and summer relative to the late fall 462 (Mouw and Yoder, 2005).

463

464 Radiocarbon ages of sediment trap material recovered from the Baltimore Canyon deep lander site 465 ranged between 980 (SD 15) and 1280 (SD 20) ¹⁴C YBP with an average age of 1096 ¹⁴C YBP 466 (SD 18) (Table 5). The most negative Δ^{14} C value (-153.75‰) occurred in the first month of the 467 deployment (September 2012), with little variability in Δ^{14} C ($\Delta\Delta^{14}$ C of 30‰) observed throughout the 468 remaining part of the year. In comparison, fresh organic matter, as defined by coral tissue Δ^{14} C values,

was 30%, consistent with surface water dissolved organic carbon Δ^{14} C values, ranging from 21 to 469 470 47‰. Therefore, the relatively "aged" material present in the trap suggests a mixture of marine and 471 terrestrial sources, as well as potential input from laterally advected refractory material (e.g., Druffel et 472 al., 1986; Gordon and Goñi, 2003; Hwang and Druffel, 2003). The aged radiocarbon dates reflect 473 organic carbon that was photosynthetically fixed thousands of years ago, such as riverine carbon 474 exported from the Hudson River Watershed that has a Δ^{14} C signature of -350% (Raymond and Bauer. 475 2001). Fingerprinting and mixing approaches have been used in submarine canyons of the 476 Mediterranean Sea to identify relative source contributions (Tesi et al., 2010; Pasqual et al., 2013). In 477 our study, results of a two end-member Δ^{14} C mixing model yielded an annual average contribution from terrestrial-derived carbon of $\sim 48\%$, with the remaining $\sim 52\%$ attributed to autochthonous organic 478 479 matter produced from marine primary production. While selective degradation/preservation can alter the source ¹⁴C signature (Hwang et al., 2010), results from the isotope mixing model are consistent 480 481 with annually averaged estimates based on molecular composition (Table 3).

482

483 Distal sources of terrestrial organic matter can be delivered via aeolian transport (Conte and Weber, 484 2002). However, surface sediment neodymium (Nd) isotope values from Baltimore Canvon and the 485 adjacent slope indicate that terrestrial sediment is primarily sourced from nearby riverine systems, such 486 as the Hudson River, where surface water moves southward, advecting riverine discharge towards 487 Baltimore Canyon and facilitating connectivity with adjacent watersheds (Ingham, 1992). Surface 488 sediments (0-0.5 cm) in the canyon were also enriched in terrestrial-derived sources of organic matter 489 relative to surface sediments on the slope (Supplementary Tables), demonstrating the accumulation of 490 terrestrial organic matter in the canyons relative to the slope. Transport of organic matter from 491 terrestrial sources is further facilitated by the presence of low-salinity, buoyant plume shelf waters on 492 the MAB (Churchill and Berger, 1998). This connectivity helps explain the terrestrial-derived organic 493 matter signature in the sediment trap samples and supports the hypothesis that submarine canyons 494 serve both as a conduit and reservoir of terrestrial organic matter to the deep sea (e.g., Tesi et al., 495 2010).

496

497 *3.3 Canyon Zonation*

498 Substantial sedimentation/turbidity events prevented the collection of a complete time series for the 499 shallow and mid-depth sediment traps, precluding a comparison amongst the three deployments. 500 However, relative changes were detected for the period of overlap during the first two months 501 (September – October) that each trap was deployed. At the shallow site, mass fluxes were the greatest 502 and ²¹⁰Pb values were the lowest among the three trap sites (Table 1b), highlighting that resuspension 503 dominates the shallow region. This is consistent with prior work demonstrating a zone of net 504 convergence where internal tides travel up and down canyon, creating a region of elevated turbidity (Gardner, 1989a, b). Within this depth zone (~ 600 m), surface sediment samples consisted of coarse 505 506 sand, small pebbles, and shell fragments at the sediment surface, presumably the result of local 507 winnowing of the surface layer removing the fines. Bulk geochemical characteristics from the shallow 508 and mid-depth traps were within the range observed at the deep site, indicating a mixture of marine and 509 terrestrial derived matter throughout the canyon. This is represented by the trap material data from the 510 shallow and mid-depth sites that plot along a mixing line, as reported above. Higher N:C ratios from 511 the shallow-depth mooring site could suggest both greater proportion of marine-derived organic matter 512 compared to the other sites and the dominance of fine-grained material in the deposition zones (Fig. 513 7b).

514

515 The relative molecular composition of the *n*-alkanes and sterols from the mid and shallow sites were 516 similar to those reported for the deep site (Table 3). For example, $n-C_{27}$ dominated the *n*-alkanes composition in the shallow and mid-depth trap sites, and cholesterol was the dominant sterol. 517 518 However, the comparison between the three sediment traps also illustrates the accumulation and 519 channeling of terrestrial organic matter farther down canyon with total *n*-alkane concentrations an 520 order of magnitude greater at the deep site relative to the shallow and mid-depth sites, particularly the 521 HMW *n*-alkanes (Table 2a). The hydrocarbons pristane and phytane were either below detection or at 522 minimal concentrations at the shallow and mid-depth sites. Total sterol concentrations during the first 523 two months were elevated at the shallow and mid-depth sites relative to the deep site, reflecting higher 524 marine-sourced sterols exported from the nutricline (e.g., cholesterol and cholestanol). While limited in 525 scope, the down canyon comparison captures spatial variability consistent with previously reported 526 canyon depth zonation patterns. In addition, relative to surface samples (0-0.5 cm) from the canyon, 527 surface samples from the adjacent slope yield lower terrestrial contribution, and an anthropogenic 528 component was absent from the slope surface sediment samples (Supplementary Table S4), supporting 529 the notion that canyons may serve as a conduit of terrestrial organic matter and contaminants. These 530 observations reflect the interplay of hydrodynamics and geomorphology, which channel and 531 concentrate sediment and organic matter within the canyon, leading to differences in organic matter 532 composition in Baltimore Canyon.

533

4. Summary

535 By examining a unique set of geochemical variables, this study demonstrated the relationship between 536 particulate matter composition in the context of seasonal variation in surface water biological 537 production and export through the nutricline in Baltimore Canyon. The sediment trap biomarker 538 compositions, together with bulk characteristics, indicate that both terrestrial OM and marine derived 539 OM are important food sources, suggesting that both vertical and lateral transport across the 540 continental margin are important processes to the deposition zone of Baltimore Canyon. However, 541 details in the temporal variability of the OM provenance reveal a larger contribution from marine-542 derived OM in the spring, which is characterized by increased scavenging, aggregation, and sinking of 543 fresh, recently exported OM from the upper water column during a spring bloom. Connectivity to 544 adjacent watershed also facilitates offshore transport of "aged" terrestrial organic matter and nutrients. 545 Results presented here demonstrate how OM content and OM provenance signature can be linked to 546 seasonal events (e.g., surface productivity blooms), episodic events (e.g., resuspension), as well as 547 those processes occurring permanent, such as the presence of the nepheloid layer. Therefore. 548 variability is a key feature influencing the deep-sea food web, with faunal composition and carbon 549 cycling influenced by seasonal or episodic fluxes in particulate matter composition. Such deposition 550 patterns in turn may be the greatest contributors to canyons exhibiting biodiversity and productivity 551 maxima. With the majority of deep-sea canyons being poorly sampled, results presented here suggest 552 that the submarine canyons of the MAB region are a key contributor to global estimates of benthic 553 biomass and productivity in the deep sea by serving as conduits for transport of terrestrial and marine 554 derived organic matter.

555 556

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- 567
- 568
- 569 Figures
- 570 **Figure 1**
- 571 Multibeam bathymetry of Baltimore Canyon showing position of benthic landers (white plus sign) and
- 572 mooring (white star) at the shallow (a), mid (b) and deep (c) sites. Progressive vector plots show the

573 cumulative movement of water at shallow (a), mid (b) and deep (c) sites, split into 60 day subsets 574 (black lines indicating Sept-Nov, green Nov-Jan, grey Jan-Mar, red Mar-May). Grey line and circles (i) 575 show the individual CTD casts that make up the transect along the axis of the canyon (two stations 576 were used for water sampling, ii=NF-2012-036 and iii=NF-2012-040) as shown in Figure 3. Black 577 triangles represent CTD casts used for water and trace element sampling (iv=NF-2012-138, v=NF-578 2012-128, vi=NF-2012-051, vii=NF-2012-130, viii=NF-2012-149, ix=NF-2012-073). Note some 579 stations are shown with an offset line for clarity. Inset figure shows the location of Baltimore Canyon 580 (black box) with respect to the Mid-Atlantic Bight and neighboring states of Maryland (MD), Virginia 581 (VA) and Delaware (DE). Contour lines show depth in meters.

582

583 Figure 2

Oceanographic variables (y-axis) recorded by the shallow lander (603 m), mid-mooring (1082 m, note no turbidity sensor) and deep lander (1318 m) in Baltimore Canyon. Black or white lines represent a 24-hour moving average. For the shallow and deep landers all sensors recorded at 1.5 m above bottom except for currents at 2 m above bottom, which were recorded at a 15 min interval. For the midmooring, current data was obtained at 14 m above bottom and temperature at 9 m above bottom. Currents were recorded at a 15-minute interval. Temperature was recorded at a 5-minute interval and was resampled to a 15-minute interval to match other sensors.

591

592 **Figure 3**

593 Baltimore Canyon nepheloid layer distribution along the canyon axis, derived from CTD profiles with 594 overlaid isopycnals (kg m⁻³). Vertical lines show the position of CTD casts along the transect, 595 including extreme margins in the plot (number of casts = 9). Turbidity expressed as relative Formazin 596 turbidity units (FTU).

597

598 Figure 4

599 Trace element concentrations ($\mu g g^{-1}$; neodymium [Nd], lanthanium [La], aluminum [Al], and iron 600 [Fe]) in suspended particulate matter filtered (>0.45 μ m) at discrete water column depths from CTD 601 casts in Baltimore Canyon and adjacent slope. Gray bar indicates zones of elevated turbidity derived 602 from CTD casts.

603

604 Figure 5

Nutrient vertical depth profiles from Baltimore Canyon sampled in 2012 along a down-canyon transect for (a) nitrate, (b) phosphate, and (c) silicate (μ mol L⁻¹) at four CTD stations, including NF12-036, NF12-040, N12-051, and NF12-073. Dissolved oxygen (black line) derived from the CTD sensor is shown for the Baltimore Canyon deep station (NF-12-040). Gray bar indicates depth of nutricline defined from nutrient profiles collected during the August 2012 sampling cruise. (d) Down canyon temperature (°C) profile derived from CTD casts.

611

612 **Figure 6**

Time-series for bulk sediment measurements and molecular biomarker composition derived from ~monthly sediment trap samples deployed from September 5, 2012 to June 23, 2013. Results are shown for (a) mass flux (g m⁻² d⁻¹) and ²¹⁰Pb (mBq g⁻¹), (b) total sterol and *n*-alkane concentration (μ g g⁻¹ C) and chlorophyll-*a* (mg g⁻¹), (c) cadmium (Cd) and molybdenum (Mo) (μ g g⁻¹), and (d) net primary production (g C m⁻² d⁻¹; http://www.science.oregonstate.edu/ocean.productivity/index.php).

618

619 **Figure 7**

(a) Stable isotope composition of carbon (δ^{13} C; ‰) versus total nitrogen:organic carbon (N:C) ratio from the deep sediment trap (1318 m) samples. The potential sources of organic carbon (C3 vascular plants, C3 soil organic matter, heterotrophic bacteria, and marine phytoplankton) are shown to highlight mixed sources of organic matter to the deep-sea sediment samples. The N:C ratio is plotted versus δ^{13} C rather than the C:N ratio because the N:C ratio behaves linearly in a mixing model (Goñi *et al.*, 2003). (b) Results from the shallow (603 m) and mid-depth (1082) sites relative to the deep site for the months of overlap (Aug-Sept. 2012).

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Figure 4



Figure 5









Start-Date	Mass Flux (g m ⁻² d ⁻¹)	N (%)	δ ¹⁵ N (‰)	C_{org} (%)	δ ¹³ C (‰)	C:N (atomic)	²¹⁰ Pb (mBq g ⁻¹)	Chl-a $(\mu g m^{-2} d^{-1})$
6-Sep-12	6.7	0.37	5	3.61	-22.4	9.8	1159	0.9
26-Sep-12	9	0.41	5	4.05	-22.5	9.9	1141	4.3
26-Oct-12	5.5	0.41	4.9	3.64	-22.0	8.8	1243	10.5
25-Nov-12	6	0.39	4.9	4.15	-22.0	10.6	1284	3.7
25-Dec-12	7.1	0.39	5	3.74	-22.2	9.6	1184	1.9
24-Jan-13	9.1	0.43	5	3.81	-22.1	8.9	1164	5.4
23-Feb-13	4.7	0.43	4.8	4.32	-22.3	10.1	1268	6
24-Apr-13	2.5	0.41	4.6	4.36	-22.2	10.5	1514	3.1
24-May-13	4	0.42	4.3	3.95	-22.8	9.3	1417	16.1
23-Jun-13	5.4	0.4	4.8	3.75	-22.4	9.4	1296	7.4

Table 1a

Mass fluxes and bulk geochemical measurements from monthly sediment trap samples deployed at 1318 m in Baltimore Canyon, Mid-Atlantic Bight.

Start-Date	Mass Flux (g m ⁻² d ⁻¹)	N (%)	δ ¹⁵ N (‰)	C_{org} (%)	δ ¹³ C (‰)	C:N (atomic)	²¹⁰ Pb (mBq g ⁻¹)	Chl- <i>a</i> (µg m ⁻² d ⁻¹)
7-Sep-12	16.5	0.39	4.9	3.73	-22.6	9.5	890	n/a
26-Sept-12	52.2	0.38	4.9	3.7	-22.2	9.7	713	n/a

Table 1b

Mass fluxes and bulk geochemical measurements from sediment trap samples deployed at 603 m in Baltimore Canyon, Mid-Atlantic Bight.

Start-Date	Mass Flux (g m ⁻² d ⁻¹)	N (%)	δ ¹⁵ N (‰)	C _{org} (%)	δ ¹³ C (‰)	C:N (atomic)	²¹⁰ Pb (mBq g ⁻¹)	Chl- <i>a</i> (µg m ⁻² d ⁻¹)
27-Aug-12	4.5	0.42	4.6	3.85	-22.2	9.1	1107	n/a
26-Sept-12	3.9	0.36	4.9	3.21	-22.1	8.9	1115	n/a

Table 1c

Mass fluxes and bulk geochemical measurements from sediment trap samples deployed at 1082 m in Baltimore Canyon, Mid-Atlantic Bight.

Start-Date	<i>n</i> -C ₁₄	<i>n</i> -C ₁₅	<i>n</i> -C ₁₆	<i>n</i> -C ₁₇	pr	<i>n</i> -C ₁₈	ph	<i>n</i> -C ₁₉	<i>n</i> -C ₂₀	<i>n</i> -C ₂₁	<i>n</i> -C ₂₂	<i>n</i> -C ₂₃	<i>n</i> -C ₂₄	<i>n</i> -C ₂₅	<i>n</i> -C ₂₆	<i>n</i> -C ₂₇	<i>n</i> -C ₂₈	<i>n</i> -C ₂₉	<i>n</i> -C ₃₀	<i>n</i> -C ₃₁	<i>n</i> -C ₃₂	Σ	CPI	P(aq)
6-Sep-12	n/d	n/d	0.1	n/d	0.09	0.27	0.12	n/d	0.14	0.1	0.16	0.15	0.43	0.36	0.38	0.69	0.46	0.57	0.19	0.19	n/d	4.19	2.42	0.4
26-Sep-12	n/d	0.04	0.03	n/d	n/d	0.08	0.03	n/d	0.04	0.03	n/d	0.06	0.5	0.3	0.7	1.56	1.94	2.55	1.75	1.32	0.53	11.43	5.26	0.09
26-Oct-12	n/d	0.02	0.05	0.03	0.03	0.02	0.07	n/d	0.06	0.04	0.07	0.08	0.07	0.13	0.09	0.15	0.06	0.1	n/d	n/d	n/d	0.97	1.24	0.68
25-Nov-12	n/d	0.02	n/d	0.01	0.01	0.02	n/d	0.03	n/d	0.19	n/d	0.27	n/a	n/a										
25-Dec-12	0.07	0.08	0.06	n/d	n/d	0.05	n/d	n/d	0.04	0.05	n/d	0.07	0.07	0.11	0.06	0.17	n/d	0.2	n/d	n/d	n/d	1.03	2.33	0.47
24-Jan-13	n/d	0.08	0.07	0.04	0.04	0.08	n/d	0.05	0.07	0.06	0.05	0.09	0.07	0.13	0.07	0.18	0.05	0.22	n/d	0.07	n/d	1.38	2.69	0.43
23-Feb-13	0.02	0.06	0.06	0.02	0.03	0.05	n/d	0.03	0.04	0.03	0.05	0.05	3.67	0.08	0.03	0.09	n/d	0.09	n/d	0.04	n/d	4.41	1.63	0.5
24-Apr-13	0.02	0.12	0.1	0.04	0.06	0.07	n/d	0.03	0.08	0.06	0.04	0.05	0.04	0.07	0.01	0.06	0.01	0.07	n/d	n/d	n/d	0.87	1.87	0.63
24-May-13	0.01	0.01	n/d	n/d	0.19	n/d	n/d	0.06	n/d	0.14	0.02	0.21	0.07	0.24	0	0.27	n/d	0.37	n/d	0.19	n/d	1.59	n/a	0.45
23-Jun-13	n/d	n/d	n/d	0.03	0.03	0.02	n/d	0.02	0.01	0.02	0.02	0.06	n/d	0.09	0.02	0.1	0.01	0.1	n/d	0.05	0.01	0.56	7.21	0.5
7-Sept-121	n/d	0.015	n/d	0.014	0.025	0.046	0.013	0.018	n/d	0.022	n/d	0.075	0.166	0.241	n/d	0.255	0.087	0.167	n/d	n/d	n/d	1.11	n/a	n/a
26-Sept-121	n/d	n/d	n/d	n/d	0.026	n/d	n/d	0.048	0.021	0.024	0.034	0.036	0.064	0.042	n/d	0.116	n/d	0.046	n/d	n/d	n/d	0.43	n/a	n/a
27-Aug-12 ²	n/d	0.008	0.004	0.007	0.018	n/d	n/d	0.006	0.009	0.01	n/d	0.025	0.049	0.072	n/d	0.1	0.049	0.06	n/d	n/d	n/d	0.4	n/a	n/a
26-Sept-12 ²	n/d	0.006	0.005	0.008	0.019	0.007	0.008	n/d	0.006	0.009	0.012	0.02	n/d	0.07	n/a	n/a								

Table 2a

Concentration of total (Σ) and select *n*-alkane concentrations normalized to organic carbon (µg g⁻¹ C), and parameters including Carbon Preference Index (CPI), and the Alkane Proxy (P_{aq}) in ~monthly sediment trap samples from the deep site (1182 m). Note: n/d=below detection limit and n/a=calculation not valid due to n/d values. $P_{aq}=(nC_{23}+nC_{25})/(nC_{23}+nC_{29}+nC_{31})$ (Ficken et al., 2000); CPI=0.5 * $[(nC_{25} + nC_{27} + nC_{29} + nC_{31})/(nC_{24} + nC_{26} + nC_{28} + nC_{30})] + [(nC_{25} + nC_{27} + nC_{29} + nC_{31})/(nC_{26} + nC_{30} + nC_{32})]$ (Bray and Evans 1961). ¹Data from the shallow (603 m) trap site. ²Data from the mid-depth (1082 m) trap site. Pr = pristane; ph = phytane

Start -Date	coprostanol	epicoprostanol	5- β -coprostanone	22-dehydrocholesterol	cholesterol	cholestanol	brassicasterol	campesterol	stigmasterol	β-sitosterol	stigmastanol	Σ
6-Sep-12	n/d	n/d	0.72	1.27	3.80	1.21	2.31	0.42	1.10	1.74	1.13	13.71
26-Sep-12	n/d	0.41	0.87	n/d	0.81	n/d	n/d	0.25	0.27	0.83	n/d	3.43
26-Oct-12	n/d	n/d	n/d	3.85	9.02	n/d	6.75	3.61	2.85	3.51	0.89	30.48
25-Nov-12	n/d	n/d	0.34	0.62	2.30	0.57	0.90	0.33	0.71	1.09	0.29	7.16
25-Dec-12	n/d	n/d	0.63	0.67	2.17	0.92	1.10	0.54	1.02	1.31	0.36	8.71
24-Jan-13	n/d	n/d	0.55	6.15	3.01	0.95	2.79	1.05	1.62	2.90	0.58	19.61
23-Feb-13	0.12	0.23	n/d	n/d	0.37	2.36	n/d	0.57	0.27	0.32	0.58	4.82
24-Apr-13	n/d	n/d	0.11	n/d	0.16	0.12	n/d	0.11	0.27	0.20	0.35	1.31
24-May-13	0.13	0.18	0.21	0.94	5.44	8.37	1.44	0.35	1.18	1.52	1.58	21.34
23-Jun-13	n/d	n/d	0.05	n/d	0.28	0.60	0.08	0.10	0.08	0.09	0.07	1.33
7-Sept-121	0.00	0.34	1.15	1.98	10.35	3.30	5.85	2.23	3.46	4.63	2.95	36.23
26-Sept-121	0.05	0.05	0.73	0.30	2.83	1.18	1.84	0.24	0.89	1.48	0.47	10.06
27-Aug-12 ²	0.09	0.00	1.07	0.53	3.99	1.78	2.87	0.38	1.40	2.20	1.46	15.77
26-Sept-12 ²	0.20	0.17	2.05	0.93	7.64	3.40	5.72	0.93	2.99	4.74	2.95	31.73

Table 2b

Concentration of total (Σ) and individual sterols normalized to organic carbon ($\mu g g^{-1} C$) in ~monthly sediment trap samples from the deep site (1182 m). Note: n/d=below detection limit. ¹Data from the shallow (603 m) trap site. ²Data from the mid-depth (1082 m) trap site.

Start -Date	%Terrestrial	%Marine	%Anthropogenic
6-Sep-12	40	55	6
26-Sep-12	76	10	14
26-Oct-12	36	63	0
25-Nov-12	35	60	5
25-Dec-12	40	53	7
24-Jan-13	33	64	3
23-Feb-13	38	55	7
24-Apr-13	60	32	8
24-May-13	26	71	3
23-Jun-13	40	55	5
7-Sept-12 ¹	37	56	7
26-Sept-12 ¹	37	55	8
27-Aug-12 ²	37	59	4
26-Sept-12 ²	31	61	8

Table 3

Major organic matter sources to the sterol and *n*-alkane molecular signatures were investigated by calculating relative proportions of marine, terrestrial higher plants, and anthropogenic/petroleum contributions. Relative contributions from natural (marine versus terrestrial) and anthropogenic organic matter *n*-alkane and sterol sources were calculated following modified designations from Pisani et al. (2013). Terrestrial organic matter composition of sediments was quantified using concentrations of odd-numbered *n*-alkanes in the C_{21} to C_{31} range as well as the sterols campesterol, stigmasterol, β -sitosterol and stigmastanol. Marine components were determined using concentrations of the sterols cholesterol, cholestanol, 22-dehydrocholesterol, and brassicasterol as well as odd- and even-numbered *n*-alkanes in the C_{14} to C_{19} range. The anthropogenic components were determined using the sterol composition of coprostanol, epicoprostanol, and 5- β -coprostanone and the isoprenoid hydrocarbons pristane and phytane.¹Data from the shallow (603 m) trap site. ²Data from the mid-depth (1082 m) trap site.

Start -Date	Al	Р	V	Cr	Mn	Fe	Cu	Zn	Sr	Мо	Cd	Cs	Ва	La	T1	Pb	Th	U
6-Sep-12	58200	837	92.9	69.6	538	33600	29.7	91.4	279	0.66	0.12	4.5	449	31.3	0.51	25.9	9.31	2.05
26-Sep-12	56800	870	92	69.4	530	32700	27.5	85.7	283	0.88	0.14	4.5	415	31.3	0.5	28	9.15	2.16
26-Oct-12	55200	886	89.3	66.9	476	31900	28.3	85	298	1.1	0.15	4.4	418	30.4	0.5	26.8	8.84	2.07
25-Nov-12	57300	841	91.6	69.4	648	3 900	28.5	85.4	298	0.79	0.13	4.5	428	32.3	0.51	28.9	9.38	2.18
25-Dec-12	57000	834	91.1	68.3	696	32800	27.9	84.6	285	0.85	0.1	4.5	424	33.4	0.51	28.6	9.65	2.13
24-Jan-13	54200	872	85.2	67.5	568	31700	25	82.8	266	0.91	0.11	4.3	386	31.6	0.48	28	9.23	2.04
23-Feb-13	56200	943	91.6	73.6	501	33100	29.1	88.9	287	0.96	0.14	4.7	422	32.8	0.5	28.4	9.25	2.16
24-Apr-13	55800	948	90.7	68.2	465	32900	30.7	89.7	318	1.4	0.23	4.7	475	32.6	0.52	29.4	9.44	2.26
24-May-13	56800	859	91.4	69.1	440	33600	30.3	86	306	1.8	0.34	4.8	469	33.5	0.53	28.9	9.3	2.18
23-Jun-13	55800	877	90.9	67.4	405	32600	30	82.5	290	0.88	0.2	4.7	466	32.4	0.5	27.1	8.81	2.04
7-Sept-121	54800	858	89.8	68.4	392	32000	26.9	82.4	264	0.97	0.13	4.4	406	33.8	0.49	23.2	9.17	2.23
26-Sept-121	51900	754	82.3	62.3	424	30500	23.4	77.7	274	0.91	0.11	4.2	408	33	0.49	23.4	9.29	2.26
27-Aug-12 ²	55500	809	90.4	66.8	447	32300	27.8	109	277	0.79	0.13	4.6	436	32.1	0.5	24.5	9.29	2.13
26-Sept-12 ²	56600	830	91.5	69.5	439	33000	29.1	83.8	276	0.77	0.16	4.7	438	32.9	0.51	25.5	9.2	2.2

Table 4

Sediment trap trace element concentrations ($\mu g g^{-1}$) in ~monthly sediment trap samples from the deep site (1182 m). Al = aluminum; Ba = barium; Cd = cadmium; Cr = chromium; Cs = cesium; Cu = copper; Fe = iron; La = lanthanum; Mn = manganese; Mo = molybdenum; P = phosphorus; Pb = lead; Sr = strontium; Th = thorium; Tl = thallium; U = uranium; V = vanadium; Zn = zinc. ¹Data from the shallow (603 m) trap site. ²Data from the mid-depth (1082 m) trap site.

	Lab ID	F Modern	Em Err	CRA	CRA error	$A_{14}C_{10}(0/2)$	Δ^{14} C error	813C(%)
Start -Date		I' WIOUEIII	TIII LII	(years)	(years)	Δ^{1} C (700)	(‰)	0 ¹⁵ C (700)
6-Sep-12	126887	0.8526	0.002	1280	20	-153.75	2.00	-21.68
26-Sep-12	126888	0.8719	0.0018	1100	15	-134.65	1.80	-21.80
26-Oct-12	126889	0.885	0.0019	980	15	-121.57	1.90	-21.58
25-Nov-12	126890	0.8744	0.0018	1080	15	-132.12	1.80	-21.56
25-Dec-12	126891	0.8713	0.002	1110	20	-135.2	2.00	-21.57
24-Jan-13	126892	0.8805	0.0028	1020	25	-126.07	2.80	-21.59
23-Feb-13	126893	0.8754	0.0019	1070	15	-131.13	1.90	-21.73
24-Apr-13	126894	0.8703	0.0019	1120	15	-136.23	1.90	-21.76
24-May-13	126895	0.8758	0.0018	1070	15	-130.77	1.80	-22.15
23-Jun-13	126896	0.8689	0.0024	1130	20	-137.55	2.40	-21.76

Table 5

Radiocarbon results from sediment trap samples from the deep site (1182 m) with fraction modern (Fm) and Fm error (\pm), with modern defined as 1950, Conventional Radiocarbon Age (CRA) and CRA age error (years), and radiocarbon (Δ^{14} C; ‰) values.

Figure S1

GC-MS total ion chromatogram (TIC) of sediment trap organic matter extracted and fractionated into F1 n-alkane fraction (131-2: 10.20.2012) and F3 sterol and fatty alcohols fraction (131-6: 2.17.2013) extracts. a. aliphatic hydrocarbons, internal standards: 5α and rostane b. fatty alcohol/sterol, internal standards: 5α -and rostan- 3β -ol.

Figure S2

Oceanographic variability in temperature, turbidity and north current speed component for the shallow lander in Baltimore Canyon across two time periods, a. October to November 2012 and b. March to May 2013. Note the mechanism, initially a high turbidity event is followed by approximately 2°C fluctuations in temperature, these spikes are associated with high current speeds.

Station	Sample Type	Depth (m)	%Corg
NF-2012-107	Surface sediment (0–0.5 cm) canyon	283	0.4
NF-2012-114	Surface sediment (0–0.5 cm) canyon	652	0.4
NF-2012-054	Surface sediment (0–0.5 cm) canyon	1180	3.9
NF-2012-065	Surface sediment (0–0.5 cm) slope	170	0.1
NF-2012-070	Surface sediment (0–0.5 cm) slope	515	0.3
NF-2012-084	Surface sediment (0–0.5 cm) slope	990	1.1
NF-2012-091	Surface sediment (0–0.5 cm) slope	1186	1.5

Supplementary Table S1

Surface (0-0.5 cm) sediment samples collected within Baltimore Canyon and adjacent slope and respective percent organic carbon (%Corg).

Sample ID	n-C ₁₄	n-C ₁₅	n-C ₁₆	n-C ₁₇	pr	n-C ₁₈	ph	n-C ₁₉	n-C ₂₀	n-C ₂₁	n-C ₂₂	n-C ₂₃	n-C ₂₄	n-C ₂₅	n-C ₂₆	n-C ₂₇	n-C ₂₈	n-C ₂₉	n-C ₃₀	n-C ₃₁	n-C ₃₂	Σ
NF-2012-107	0.49	1.59	0.81	0.78	0.25	1.2	0.44	1.59	1.54	1.32	n/d	0.71	n/d	n/d	n/d	0.61	n/d	0.39	n/d	n/d	n/d	11.03
NF-2012-114	1.96	n/d	3.02	2.65	1.39	2.43	n/d	6.84	4.99	4.79	5.62	13.22	19.32	38.55	44.79	68.61	51.06	71.75	34.55	49.19	14.37	437.71
NF-2012-054	0.12	0.38	0.3	0.43	0.26	0.38	0.32	1.13	0.58	0.63	0.36	0.35	n/d	0.66	0.48	1.08	n/d	0.98	n/d	0.31	n/d	8.19
NF-2012-065	7.38	7.89	4.95	3.9	n/d	4.35	n/d	5.41	5.35	n/d	n/d	n/d	n/d	4.05	n/d	43.28						
NF-2012-070	n/d	2.37	2.16	n/d	n/d	2.13	n/d	3.59	3.46	2.67	1.74	n/d	2.41	2.76	n/d	23.29						
NF-2012-084	n/d	n/d	13.27	n/d	n/d	18.81	n/d	32.49	30.48	n/d	95.04											
NF-2012-091	0.34	n/d	1.19	n/d	n/d	1.1	n/d	1.88	n/d	4.51												

Supplementary Table S2

Concentration of total (Σ) and select *n*-alkane concentrations normalized to organic carbon ($\mu g g^{-1} C$) in surface (0-0.5 cm) sediment samples in Baltimore Canyon and adjacent slope. Note: n/d=below detection limit

Sample ID	coprostanol	epicoprostanol	5- β - coprostanone	22-dehydrocholesterol	cholesterol	cholestanol	brassicasterol	campesterol	stigmasterol	β-sitosterol	stigmastanol	Σ
NF-2012-107	n/d	n/d	n/d	n/d	1.4	0.76	1.04	3.84	0.75	0.8	0.49	9.08
NF-2012-114	n/d	0.24	n/d	n/d	1.47	2.98	1	2.42	1.21	1.24	n/d	10.56
NF-2012-054	n/d	n/d	n/d	n/d	0.94	0.49	0.87	0.78	0.08	1.26	0.35	4.78
NF-2012-065	n/d	n/d	n/d	n/d	2.6	0.87	n/d	13.1	4.39	1.5	2.13	24.59
NF-2012-070	n/d	n/d	n/d	n/d	2.38	1.21	1.31	2.08	1.36	1.18	1.42	10.95
NF-2012-084	n/d	n/d	n/d	n/d	n/d	n/d	n/d	n/d	n/d	n/d	n/d	n/d
NF-2012-091	n/d	n/d	n/d	n/d	n/d	n/d	n/d	n/d	n/d	n/d	n/d	n/d

Supplementary Table S3

Concentration of total (Σ) and individual sterols normalized to organic carbon ($\mu g g^{-1} C$) in surface (0-0.5 cm) sediment samples in Baltimore Canyon and adjacent slope. Note: n/d=below detection limit

Site	%Terrestrial	%Marine	%Anthropogenic
NF-2012-107	46	50	4
NF-2012-114	91	8	1
NF-2012-054	54	42	5
NF-2012-065	40	60	0
NF-2012-070	43	57	0
NF-2012-084	n/a	n/a	n/a
NF-2012-091	n/a	n/a	n/a

Supplementary Table S4

Major organic matter sources to the sterol and *n*-alkane molecular signatures were investigated by calculating relative proportions of marine, terrestrial higher plants, and anthropogenic/petroleum contributions in surface sediment samples in Baltimore Canyon and adjacent slope. Relative contributions from natural (marine versus terrestrial) and anthropogenic organic matter *n*-alkane and sterol sources were calculated following modified designations from Pisani et al. (2013). Terrestrial organic matter composition of sediments was quantified using concentrations of odd-numbered *n*-alkanes in the C_{21} to C_{31} range as well as the sterols campesterol, stigmasterol, β -sitosterol and stigmastanol. Marine components were determined using concentrations of the sterols cholesterol, cholestanol, 22-dehydrocholesterol, and brassicasterol as well as odd- and even-numbered *n*-alkanes in the C_{14} to C_{19} range. The anthropogenic components were determined using the sterol composition of coprostanol, epicoprostanol, and 5- β -coprostanone and the isoprenoid hydrocarbons pristane and phytane. *Note:* n/a=Source contributions were not calculated due to non-detect sterol and select*n*-alkane concentrations (*Table S2*).



Time (mins)

