



Very low sulfur fuel oil spilled from the MV *Wakashio* in 2020 remains in sediments in a Mauritius mangrove ecosystem nearly three years after the grounding

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ARTICLE INFO

Keywords:

ADIOS
VLSFO
IMO-2020
Heavy fuel oil
GC×GC
Biomarkers

ABSTRACT

The oil spill resulting from the grounding of the MV *Wakashio* on a reef off the coast of Mauritius in July 2020 was the world's first major spillage of Very Low Sulfur Fuel Oil (VLSFO) since the implementation of a Global Sulfur Cap from January 2020. In this study, we examine sediments collected in March 2023 from two Mauritius mangrove systems. Analyses by both gas chromatography–mass spectrometry and comprehensive two-dimensional gas chromatography confirmed, by comparison of molecular biomarkers, the presence of *Wakashio* VLSFO in one of the mangrove systems. The spilled oil had undergone extensive weathering resulting in substantial losses of toxic mono- and polycyclic aromatic compounds. Applying WebGNOME-ADIOS oil spill models to compare the fate of *Wakashio* VLSFO with traditional fuels suggests that more of the VLSFO would evaporate, naturally disperse, and undergo sedimentation compared to traditional fuels that were more likely to remain floating.

1. Introduction

Despite high-profile international media coverage and potential health, social, environmental, and economic impacts on Mauritius following the 2020 MV *Wakashio* oil spill, there is very limited scientific research/data accessible on the chemical composition and fate of the spilled oil beyond the analyses of the source oil and one field sample collected three weeks after the grounding (Scarlett et al., 2021). When the MV *Wakashio* struck a reef off the southeast coast of Mauritius in July 2020, the resulting 1000 t of oil spilled might be considered unexceptional by comparison with previous tanker spills of heavy fuel oils (HFO). For example, the 63,000 t of HFO spilled from the tanker *Prestige* off the coast of Galicia, Spain, in 2002 (ITOPF, 2023), was orders of magnitude larger. In addition, the *Wakashio* spill did not appear to cause any major damage to sensitive ecosystems, although this may simply be due to the lack of reported studies carried out following the *Wakashio* spill. However, this was the world's first large spillage (defined as >700 t, (ITOPF, 2023)) of Very Low Sulfur Fuel Oil (VLSFO) since the International Maritime Organization (IMO) implemented the Global Sulfur

Cap regulation in January 2020 (IMO, 2020; Scarlett et al., 2021). The new IMO regulation aimed to reduce air pollution by limiting emissions of sulfur-oxide (SO_x) and nitrous-oxide (NO_x) compounds and particulates from shipping (ocean-going vessels). Colloquially known as IMO-2020, the regulations lowered the allowable weight percentage of sulfur in marine fuel oils to 0.5 wt% down from 3.5 wt%, although ships can continue to burn traditional HFOs, such as Intermediate Fuel Oil (IFO) 180 and Bunker C, if scrubbers are used to remove sulfur from engine exhausts (IMO, 2020). The IMO-2020 regulation appears to be achieving its aim: ship tracks defined by aerosol emissions from ships' exhausts are reported to have fallen significantly following the implementation of IMO-2020, although a reduction in shipping resulting from economic disruption caused by the Covid-19 pandemic would have contributed to this (Yuan et al., 2022).

The United States, Canada, and some European Union countries have implemented more stringent Sulfur Emission Control Areas (SECAs) requiring Marine Operators to utilize marine fuels containing a maximum of 0.1 wt% sulfur (CARB, 2020) in certain zones. Marine fuels meeting this sulfur requirement are known as Ultra Low Sulfur Fuel Oil

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<https://doi.org/10.1016/j.marpolbul.2024.117283>

Received 23 May 2024; Received in revised form 6 November 2024; Accepted 8 November 2024

Available online 18 November 2024

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(ULSFO). Nelson et al. (2022) reported that two ULSFOs obtained from different sources, and from different areas of the world, were near identical and could easily be differentiated from three VLSFOs, including that from the *Wakashio*. There remains very little information about the behavior of VLSFOs and ULSFOs in the environment, although the physical properties of some IMO-2020 and SECA-compliant oils have been thoroughly investigated (Sørheim et al., 2020, 2021). These studies have helped us understand how these oils may differ from traditional HFOs and how they may best be tackled when spilled, including how they interact with chemical dispersants (Sørheim et al., 2020, 2021).

The immediate response to the *Wakashio* spill was partly organized by local citizens, e.g., by constructing make-shift booms from palm leaves to prevent the oil from coming ashore. Since the spill, there have been no official reports of oil reaching sensitive ecosystems despite local people claiming that oil is present in the mangrove systems. These ecosystems are reported to be highly vulnerable to oil pollution in part due to chronic exposure to hydrocarbons (Lassalle et al., 2023; Lewis and Pryor, 2013). Satellite and aerial images have been used to track the movements of the spilled oil released from the *Wakashio* as it was pushed by the trade winds towards coral reefs and the shoreline (Rajendran et al., 2022; Rajendran et al., 2021; Sunkur and Bokhoree, 2021) but physical evidence of contamination of sediments, plants and animals is still lacking in published literature.

At the time of the *Wakashio* oil spill there was much confusion in the media about the composition of spilled material. However, analysis of *Wakashio*'s fuel and a field sample revealed that it was a VLSFO and not mixed with other oils on board the vessel (Scarlett et al., 2021). It has also been demonstrated that the *Wakashio* fuel oil could be readily differentiated from two other VLSFOs (Nelson et al., 2022). An analysis of sediments collected in March/April 2022 from several Mauritius coastal locations, including mangrove areas, revealed <5 to >4000 mg kg⁻¹ of total petroleum hydrocarbons (TPH; unpublished data). While suspected to be associated from the *Wakashio* oil spill, the source(s) of the hydrocarbons was not established. Understanding how far the oil may have travelled following the spill and which ecosystems and communities may have been impacted is crucial for clean-up strategies, future monitoring, restoration, and economic compensation for people affected by the spill. In addition, because so little is known about the behavior of IMO-2020-compliant oils, this virtual vacuum of information regarding the aftermath of the *Wakashio* spill has consequences globally on how to plan and respond to future spills of VLSFO.

The behavior of VLSFOs during and after a spill can be compared to HFOs using models. For example, Sørheim et al. (2021) used an Oil Weathering Model to compare IM-5 *Wakashio* oil with two VLSFOs, and two ULSFOs over a seven-day period in cold-climate conditions (2 °C and 15 °C). Temperature has a large impact on the outcome of the model's result, as indeed it does in real environmental spills (Freeman et al., 2023). Hence, exploring the predicted differences between a traditional HFO and the *Wakashio* VLSFO in terms of the relative amounts of oil floating, evaporated, dispersed etc., and the corresponding changes to density and viscosity, over a period of weeks, simulating the environmental conditions following the spill in Mauritius could provide useful insight. In addition, this modeling could prove useful for planning how to respond to any future spills of VLSFO in tropical waters. Subsequent comparisons with empirical data from environmental spills could help validate the models.

In the current study, we compare sediments sampled from two mangrove systems in the southeast of Mauritius in March 2023 with that of the *Wakashio* fuel oil and a sample of the spilled oil collected three weeks after the grounding i.e. within days of the spill commencement (Scarlett et al., 2021). Gas Chromatography – Mass Spectrometry (GC–MS) was used to perform forensic ‘fingerprinting’ by examination of a number of non-volatile terpenoid biomarkers (biological markers associated with petroleum origin) highly resistant to biodegradation. Further examination of the sediment and oil samples were performed by comprehensive two-dimensional gas chromatography - flame ionization

detection (GC×GC-FID) such that comparisons could be made with previous studies (Nelson et al., 2022; Scarlett et al., 2021). The aim of the forensic study was to confirm or refute the assumption that fuel from the *Wakashio* was present in a Mauritius mangrove system nearly three years after the spill. The study was not designed to be quantitative or to assess the risk posed by the presence of oil. In an additional aspect of the study, we use the ADIOS oil database and weathering models, which is now incorporated in the National Oceanic and Atmospheric Administration's (NOAA) WebGNOME suite (<https://response.restoration.noaa.gov/webgnome>), to compare the weathering and fate of *Wakashio* VLSFO, an IFO 180 and a Bunker C fuel oil under typical environmental conditions prevailing at the time of the *Wakashio* oil spill. The aim of this part of the study was gain insight into the possible different behavior of the VLSFO spilled and that of non-IMO-2020-compliant oils.

2. Materials and methods

2.1. Samples

Three sediment samples from each of two stations, M1 and M0, were collected in late March 2023 from the south-eastern coast of Mauritius at locations S20.37154°, E051.71163° and S20.39410°, E057.70050° for M1 and M0 respectively. Sediments from the vicinity of M1 location (Supplementary Information Fig. S1), sampled and analyzed in early 2022, had previously been found to contain high concentrations of total petroleum hydrocarbons (TPH >4 g kg⁻¹, unpublished data). The hydrocarbons detected at site M1 were suspected to have originated from the *Wakashio*, whereas site M0 appeared to be uncontaminated by petroleum hydrocarbons (TPH <0.005 g kg⁻¹, unpublished data) (Supplementary Information Fig. S1). The sediment samples plus an empty jar were couriered to the Western Australian Organic and Isotope Geochemistry Centre (WAOIGC) laboratories and were immediately placed in cold storage until extraction the following day.

A field sample of spilled oil, collected on 16th August 2020 from S20.39714°, E57.69953° plus fuel oil from the MV *Wakashio* were available from a previous study (Scarlett et al., 2021).

2.2. Extraction and fractionation of sediments

Glassware was soaked in Mucosal® (Sigma-Aldrich, Steinheim, Germany) for >2 h, rinsed with deionised water and heated to 500 °C for 2 h. Solvents were HPLC grade or higher (Honeywell Burdick & Jackson®, Muskegon, MI, USA).

Upon opening the jars, an oily smell was observed for all sediment samples collected at M1 but not M0. For each replicate jar, the sediments were homogenized by stirring with a stainless-steel spatula. From each jar, ~10 g of sediment was transferred to clean beakers with 10 mL 7:3 *n*-hexane:dichloromethane (DCM). The supplied empty jar was rinsed with *n*-hexane:DCM (10 mL). This was used to provide a procedural blank for background, handling, and transport in Mauritius along with the extraction, fractionation and concentration in the laboratory. The beakers were covered in aluminium foil and sonicated for 15 mins. The solvent extract (bitumen) was treated with copper turnings to remove elemental sulfur, filtered through a bed of anhydrous MgSO₄, to remove particulate and dry, reduced in volume with a gentle stream of nitrogen and weighted to determine the total solvent extractable material. Aliquots of the bitumen extracts (<10 mg) were loaded onto small silica columns (Merck silica gel pre-rinsed with *n*-hexane) to obtain saturated hydrocarbon fractions. The columns were prepared in glass Pasteur pipettes with 0.5 g of pre-activated silica gel *n*-hexane slurry. The saturated hydrocarbon fraction was eluted with 3 mL of *n*-hexane and the aromatic fraction with 3 mL 7:3 *n*-hexane:DCM then evaporated under a gentle nitrogen stream. The fractions were diluted or concentrated as required for analysis by GC–MS conducted at the WAOIGC laboratories. The extraction procedure was repeated but without fractionation and shipped to Woods Hole Oceanographic Institution, USA for GC×GC-FID

analysis.

2.3. Analyses of sediment extracts by GC–MS

In order to compare the sediment extracts with the VLSFO obtained from the *Wakashio* after the grounding, recalcitrant terpenoid biomarkers were targeted for GC–MS analysis (Aeppli et al., 2014; Scarlett et al., 2021; Stout, 2016).

Saturated hydrocarbon fractions of the sediment bitumen extracts and fuel oil from the *Wakashio* were analyzed using a HP-6890B gas chromatograph (Agilent, Santa Clara, CA, USA) interfaced to a HP-5977B mass selective detector (Agilent). The GC was fitted with a DB-1ms capillary column (60 m × 0.25 mm internal diameter × 0.25 µm film thickness). Aromatic fractions were analyzed on an Agilent 6890 N GC coupled to a 5975B MSD, using a DB-5ms UI column (60 m, 0.25 mm i.d., 0.25 µm film thickness). For both fractions, 1 µL of solution was injected into a split/splitless injector operating in pulsed splitless mode, held at 280 °C, with high purity helium carrier gas at a constant flow of 1.1 mL min⁻¹. The GC ovens were programmed from 40 °C (held 1 min) to 325 °C at 3 °C min⁻¹ with a final hold time of 30 min. The MSDs were operated at 70 eV with a source temperature of 230 °C. Mass spectra were acquired in full scan mode from 50 to 600 Da and with selected ion monitoring (SIM) for saturates: *m/z* 123, 191, 205, 217, 218, 358, 370, 372, 384, 386, 398, 400, 412, 414, 426, 428, 440, 442, 454, 456. Identification of terpenoid biomarkers was aided by reference to certified analytical standards (NIST SRM-2266, Gaithersburg, MD, USA). Ratios used for forensic examples of samples are provided in Supplementary Information Table 1. SIM ions monitored for aromatic hydrocarbons were: *m/z* 107, 121, 128, 133, 134, 135, 142, 149, 152, 153, 154, 156, 159, 161, 166, 168, 170, 173, 175, 178, 182, 183, 184, 188, 189, 192, 197, 198, 202, 206, 211, 212, 216, 219, 220, 228, 231, 233, 234, 237, 248, 251, 252, 253, 266, 268, 276, 278, 282, 300, 302, 386, 400, 414. Identification of aromatic compounds was by reference to certified analytical standards (Neochema, Bodenheim, Germany). Data was processed using ChemStation (Agilent) software. The GC–MS was operated according to standard laboratory quality controls such as background air and water checks, tuning and regular checking of instrument performance using test mixtures of analytic standards and SRM-1582 (Petroleum Crude Oil). The calculation of biomarker ratios, statistical operations, and data visualization were performed using Excel (Microsoft).

2.4. Analyses of sediment extracts by GC×GC-FID

GC×GC-FID chromatographic analyses were performed on a LECO system consisting of an Agilent 7890A GC configured with a split/splitless auto-injector (7683B series) and a dual stage cryogenic modulator (LECO, Saint Joseph, Michigan). Samples were injected in splitless mode. The cold jet gas was dry N₂ chilled with liquid N₂. The hot jet temperature offset was 15 °C above the temperature of the main GC oven and the inlet temperature was isothermal at 310 °C. Two capillary GC columns were utilized in this GC×GC experiment. The first-dimension column was a Restek Rxi-1ms, (60 m length, 0.25 mm I.D., 0.25 µm df) and second-dimension separations were performed on a 50 % phenyl polysilphenylene-siloxane column (SGE BPX50, 1.2 m length, 0.10 mm I.D., 0.1 µm df). The temperature program of the main oven was held isothermal at 55 °C (12.5 min) and was then ramped from 55 to 330 °C at 1.25 °C min⁻¹. The second-dimension oven was isothermal at 60 °C (12.5 min) and then ramped from 60 to 335 °C at 1.25 °C. The hot jet pulse width was 1 s, while the modulation period between stages was 8 s and a 3 s cooling period between stages. FID data was sampled at an acquisition rate of 100 data points per second. ChromaTOF (LECO) software package was used for instrument control and data analysis. GC×GC-FID performance was monitored using SRM-1582 for calibration and validation. This standard oil was routinely interspersed with analytical samples to monitor a suite of biomarker ratios in order to

confirm that the instrument was stable and operating normally.

2.5. ADIOS model parameters

WebGNOME-ADIOS provides an interface for modeling oil spill scenarios in which users can set up a custom spill scenario, run the model, and visualize the results including a full oil weathering analysis (<https://response.restoration.noaa.gov/oil-and-chemical-spills/oil-spills/webgnome>). WebGNOME-ADIOS is designed primarily for the modeling of surface fate and transport and therefore does not predict biodegradation within sediments. Additional properties of the oils modelled e.g. viscosities, densities, bulk composition, compounds etc., and the original source of the data can be freely accessed at <https://adios.orr.noaa.gov/oils> using the ADIOS reference numbers provided below.

The oils used in the models were VLSFO IM-5 (IMAROS; ADIOS reference ID: AD0259), which was the *Wakashio* fuel oil (American Petroleum Institute (API) gravity 24.2, pour point 9 °C), a HFO non-compliant with IMO-2020, Bunker C (ADIOS reference ID: AD00208) which was chosen as it is an unusually light and low viscosity oil for a Bunker C oil i.e. more closely resembling the *Wakashio* fuel oil (API 13.7, pour point 15 °C) and IFO 180 (ADIOS ID: EC01955; API gravity 14.8, pour point 15 °C). This IFO 180 has a reported *n*-alkane range of *n*-C₉ to *n*-C₄₀ (<https://adios.orr.noaa.gov/oils/EC01955#ember27477>) which is very similar to that reported for the *Wakashio* fuel oil (Scarlett et al., 2021). Water temperature was set at 23 °C, the average sea temperature for early August in Mauritius (available: <https://www.seatemperature.org/africa/mauritius/> accessed 09 April 2024). The wind speed was set at a constant 20 knots, which is typical for wind speed for trade winds in the area of the grounding, but in reality, the wind would have varied somewhat. The wave height was computed from wind speed. The total amount of oil spilled was set at 1000 t beginning on the 6th August and lasting until the ship broke up on 15th August 2020, hence nine days. The release was set at ‘continuous’, giving a spill rate of 4.63 t per hour. It is likely that the spill rate would have changed as the ship shifted on the reef and other factors but these are unknown. The total spill scenario duration, i.e. the time the model ran, was 30 days from commencement of the spill.

2.6. Statistical comparison of biomarker ratios

Daling et al. (2002) suggested that for correlations between spilled and source oils that if the 95 % Confidence Intervals (CI) of all key diagnostic ratios resistant to weathering (e.g. sterane and hopane biomarkers) cross the ideal 1:1 relationship, this should be classed as a positive match. If all fall within the 98 % CI, this should be classed as a probable match, but if any key diagnostic ratio falls outside the 98 % CI, this should be classed as a non-match. Given the high degree of weathering observed in the chromatograms of the sediment organic extracts, a comparison was made between 20 ratios (derived by GC–MS) of mostly pentacyclic terpanes that are highly resistant to weathering and biodegradation (Table S1). If a biomarker ratio derived from M1 fell within the 95 % confidence limits of those derived from the *Wakashio* fuel oil it was declared a ‘match’. A summary of the means and 95 % CI for each biomarker is provided in Table S1.

3. Results and discussion

3.1. Forensic comparison of biomarkers present in sediment extracts by GC–MS

The total bitumen extracts of all three samples from M0 contained very little organic content by weight (~0.03 g kg⁻¹) and had to be highly concentrated to detect any hydrocarbon peaks by GC–MS analysis (Supplementary Information Fig. S2). There was no indication of hydrocarbon contamination from crude or fuel oil and no terpenoid biomarkers were detected in these extracts. No contamination was evident

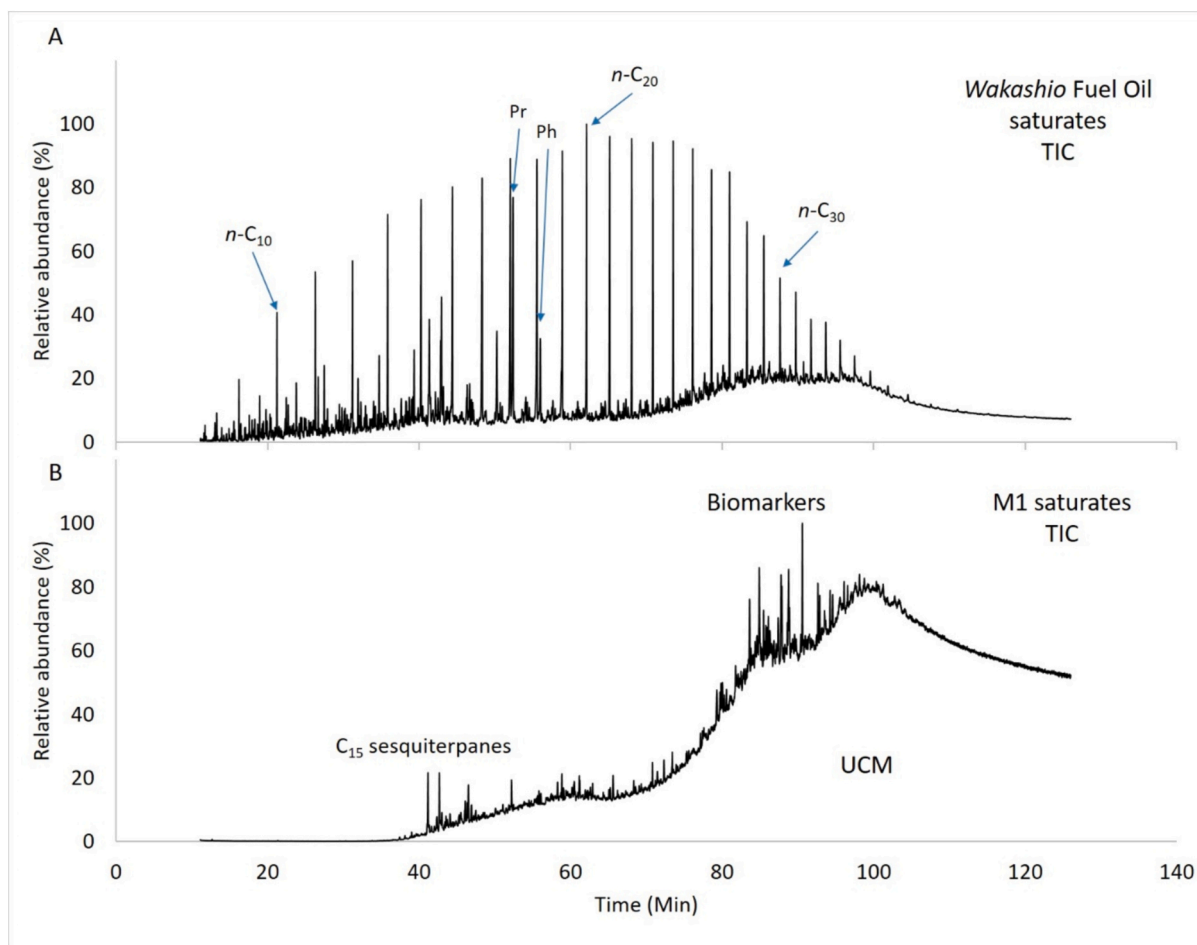


Fig. 1. Full Scan GC-MS Total Ion Chromatograms (TIC) of saturates fraction of (A) fuel oil from the MV *Wakashio* and (B) an organic extract of sediment from a mangrove system collected in March 2023 in Mauritius (M1). Peaks corresponding to recalcitrant biomarker hydrocarbons are prominent above an unresolved complex mixture (UCM) of hydrocarbons in M1.

and no biomarkers were detected in the procedural blank. In contrast, the extracts obtained from all three sediment samples from M1 contained a very large organic component (mean 16.1 g kg^{-1} , standard deviation 0.66 g kg^{-1} , $n = 3$).

Full scan Total Ion Chromatograms (TIC) of all three sediment sample extracts from M1 revealed large unresolved complex mixtures of hydrocarbons (UCM) with only peaks of the more recalcitrant chemical structures, such as some isoprenoids, bicyclic sesquiterpanes, steranes and hopanes, visible above the UCM, which is consistent with contamination from biodegraded oil. An example comparison of saturate fractions of the *Wakashio* fuel oil and one of the sediment extracts is shown in Fig. 1. Volatile hydrocarbons that are typically present in fresh crude/fuel oils were absent, as were readily biodegraded hydrocarbons such as *n*-alkanes (Fig. 1B). Many terpenoid biomarkers previously observed in VLSFO from the MV *Wakashio* (Scarlett et al., 2021) were present in all three M1 samples. Using GC-MS SIM analysis, the terpenoid biomarkers were more readily visualized (Fig. 2). Diagnostic ratios of the biomarkers were quantified and compared with those of the *Wakashio* VLSFO.

Ratios of terpenoid biomarkers obtained from the sediment extracts from site M1 were similar to those obtained from the *Wakashio* VLSFO (Scarlett et al., 2021) (Supplementary Information Table S1). A cross-plot of terpenoid biomarker ratios obtained from site M1 sediment extracts and those from the *Wakashio* VLSFO is shown in Fig. 3. Linear regression of terpenoid biomarker ratios derived from sediments and fuel oil produced a relationship of $y = 0.9884x + 0.0057$ with r^2 of 0.9995 (Fig. 3). The cross-plot revealed that the terpenoid biomarker

ratios all plotted very close the ideal 1:1 line and that all 95 % confidence intervals crossed the 1:1 line indicating a positive match (sensu Daling et al., 2002) between the saturated hydrocarbon fraction extracted from sediments collected at location M1 and the *Wakashio* VLSFO. A statistical comparison of 20 ratios derived from M1 and *Wakashio* fuel oil found a positive match for all except three ratios (Table S1). Examination of the non-matching ratios revealed that for two of the ratios, the mean values were virtually identical for both sediment M1 and the *Wakashio* fuel oil. For example, the ratio NH/H was 0.557 and 0.562 for M1 and *Wakashio* respectively (Table S1) and the reason for the non-match was simply due to extremely small 95 % confidence limits. This was also the case for the ratio C32S/C32S+R. For both ratios, those for M1 were well within the 98 % CI (0.03 and 0.065 for NH/H and C32S/C32S+R respectively) of the *Wakashio* fuel oil ratios (Table S1). The mean ratio M/H of 0.07 for M1 was just outside the 95 % CI for the ratio derived from the *Wakashio* fuel oil (mean 0.10 ± 0.02) but inside the 98 % CI (0.05). Overall, there was clearly a significant positive match between biomarker ratios derived from sediment M1 and that of the *Wakashio* fuel oil (Fig. 3, Table S1). With oil-spill fingerprinting being far from an exact science, largely stemming from the petroleum industry and select oil spills with samples collected within days and weeks after a release, it is quite remarkable that three years after the *Wakashio* oil spillage, in a tropical location, that such a positive match could be achieved. Although no baseline data for hydrocarbons present in the mangrove sediments was available, the minimal variation in the M1 sediment biomarkers suggests that this location was completely pristine at least with regards to oil contamination. There was no

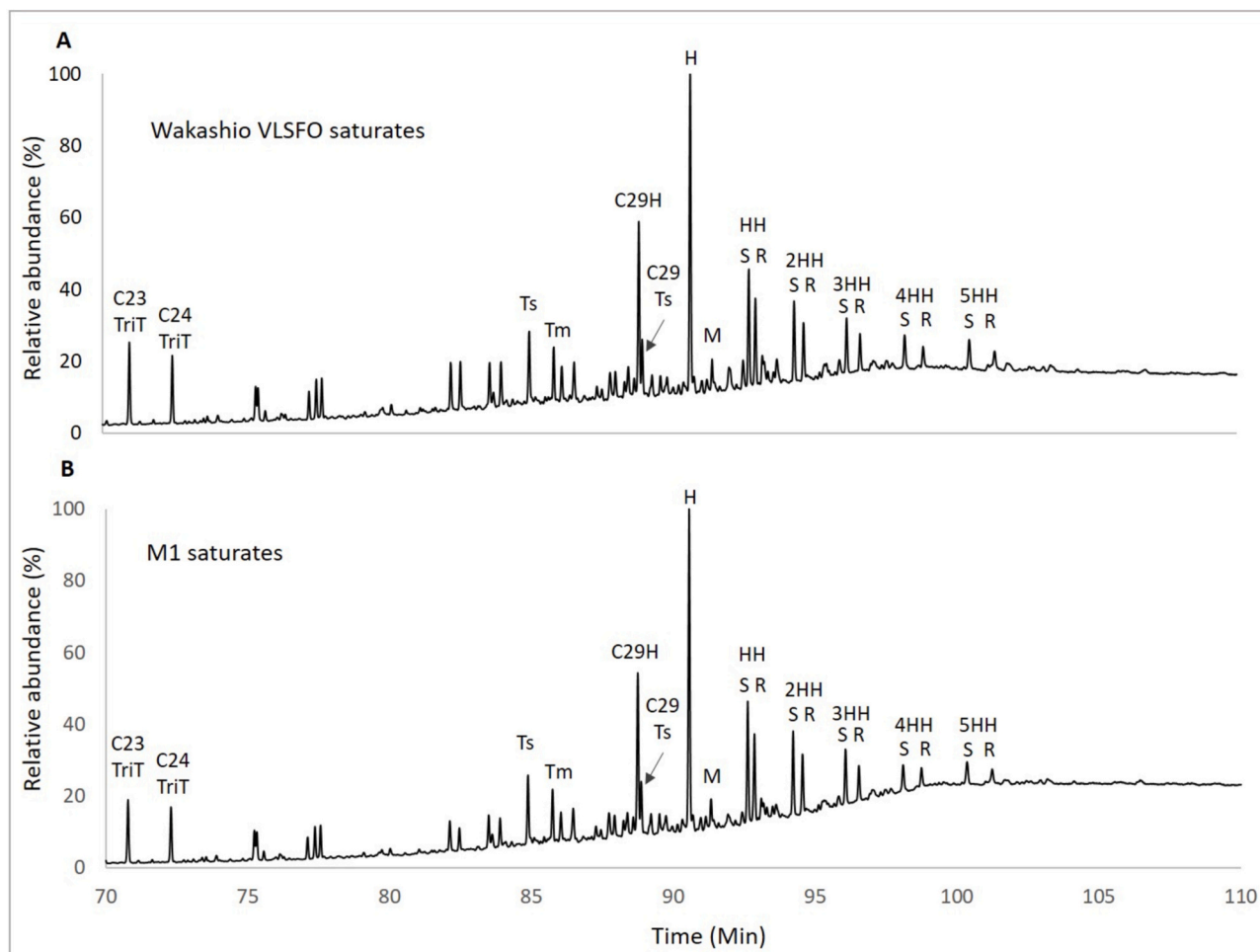


Fig. 2. Selected Ion Monitoring GC-MS Extracted Ion Chromatogram (m/z 191) of saturates fraction biomarker region of (A) the *Wakashio* fuel oil and (B) an organic extract of sediment from a mangrove system in Mauritius (M1). Acronym definitions of biomarkers are provided in Appendix 1.

indication of any oil contamination by VLSFOs or other petroleum hydrocarbons at location M0.

To provide additional confidence to the GC-MS SIM results and to investigate what other compounds remained by resolving the UCM, sediment extracts were analyzed by GC \times GC-FID. The increased resolution across the boiling range and polarity of hydrocarbons provide valuable insights into weathered and biodegraded oils (Frysiner et al., 2003; Gaines et al., 1999; Nelson et al., 2016; Nelson et al., 2006; Rowland et al., 2011; Scarlett et al., 2019).

3.2. Comparison of *Wakashio* fuel oil, spilled oil and sediment samples by GC \times GC-FID

GC \times GC-FID chromatograms of the VLSFO from the *Wakashio* and sediment extract from M1 are shown in Fig. 4 and highlight the broad-scale difference in the hydrocarbon content. A difference chromatogram (Fig. 4C) provides a visual accounting of weathering. Compounds lower or higher in relative abundance are easily observed (Fig. 4). It is seen in the sediment extract chromatogram (Fig. 4B) that there are fewer prominent peaks with high abundances. Of these, chemical structures that are resistant to weathering processes are dominant, e.g. the isoprenoids pristane and phytane, bicyclic sesquiterpanes such as drimane and homodrimane, steranes such as the diasterane 13 β (H),17 α (H)-20S-diacholestane (C₂₇H₄₈) and numerous hopanes (Fig. 4, Supplementary Information Fig. S3). The difference chromatogram (Fig. 4C) shows compounds that are relatively decreased in blue, those with a relative increase in red and those unchanged in white i.e. they appear to vanish

against the background. As the difference chromatogram has been normalised to 17 α (H),21 β (H)-hopane (C₃₀H₅₂), it is clear that no compound has increased in abundance relative to hopane. The vast majority of compounds, including many of the recalcitrant compounds listed above, appear blue indicating their relative loss (Fig. 4C). The hopanoid biomarkers appear white in the difference chromatogram indicative of their resistance to biodegradation. Comparisons of biomarker regions for all three sediment extracts from station M1 appear identical to each other (Supplementary Information Fig. S4) and to that previously reported for the *Wakashio* fuel oil and spilled oil (Scarlett et al., 2021), indicating that the oil derived from the *Wakashio* spill is homogenous in the mangrove sediments rather than isolated pockets at location M1 and that no other oil contamination is present.

It was previously observed that the *Wakashio* VLSFO had unusually low Polycyclic Aromatic Compounds (PAC) content when compared to 71 HFOs and with other VLSFOs (Nelson et al., 2022; Scarlett et al., 2021; Uhler et al., 2016). Comparing the aromatic region of the GC \times GC-FID chromatograms (Fig. 4, Supplementary Information Fig. S5), it can be seen that most of the monoaromatic hydrocarbons and PACs have decreased in abundance and many have been lost entirely. Some three-ringed PACs remained with a shift towards an increased relative abundance of structures with greater alkylation. For example, the *Wakashio* fuel oil was reported to have a dominant phenanthrene peak with decreasing relative abundance of alkyl-phenanthrenes with increasing alkylation, but the sediments at M1 were dominated by C₃ and C₄-phenanthrenes (Supplementary Information Fig. S6). This was also observed using GC-MS SIM analysis of the aromatic fraction

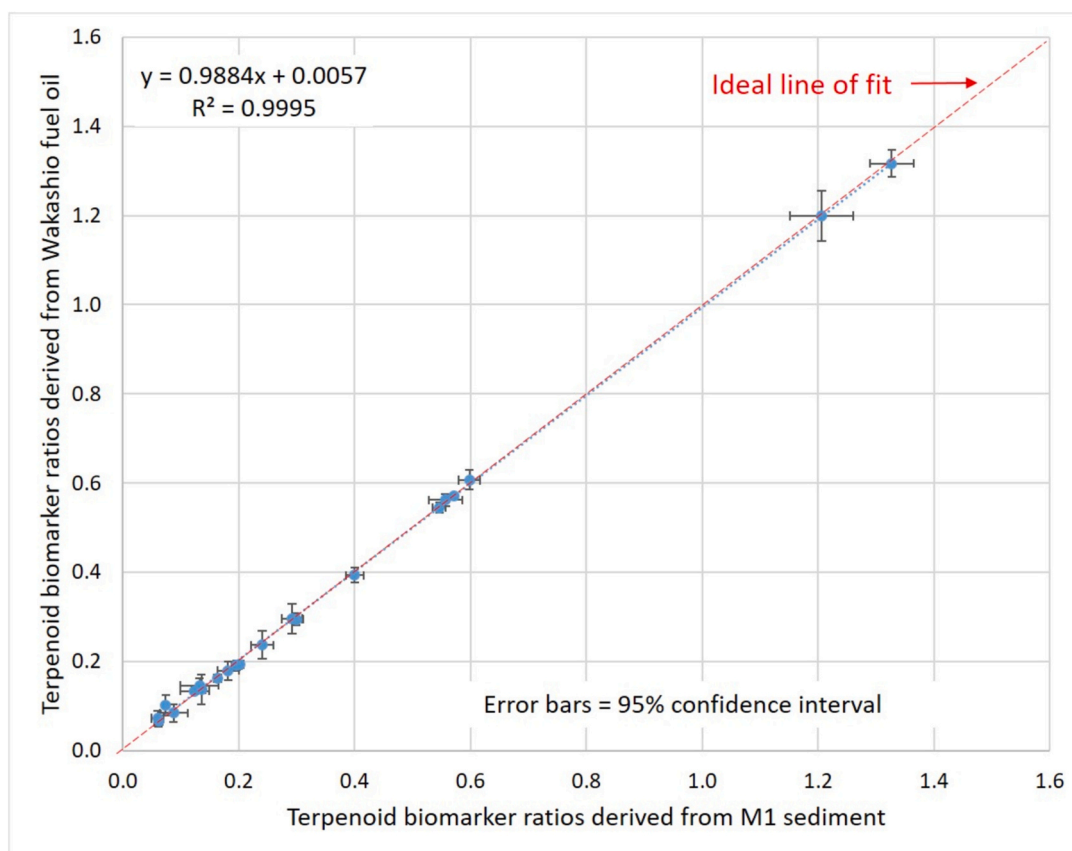


Fig. 3. Cross-plot of terpenoid biomarkers ratios obtained from mangrove site M1 sediment extracts and those from the *Wakashio* VLSFO. Error bars indicate 95 % confidence intervals. Mean biomarker ratio values and their 95 % confidence limits are provided in Table S1.

(Supplementary Information Fig. S7). The parent structure of phenanthrene has been shown to impact fish embryonic cardiac function and development through direct blockade of K^+ and Ca^{2+} currents that regulate cardiomyocyte contractions independent of the aryl hydrocarbon receptor (AHR), whereas increasing alkylation has been reported to produce AHR activation with various effects dependent upon the pattern of alkylation (Incardona et al., 2024). Although some higher weight (4 and 5 ring) PACs were still detectable in the sediment extracts, these have limited bioavailability and it has become increasingly evident that 3-ring PACs pose to greatest risk to fish (Brette et al., 2017; Incardona et al., 2004; Incardona et al., 2024). In order to ascertain the degree to which the C_1 and C_2 -alkylphenanthrenes have been lost since the oil spill, we compared their hopane-normalised concentrations using GC×GC-FID. This revealed a pronounced decline in their abundance in the spilled oil compared to the fuel. The ratio of ΣC_1 -phenanthrenes/hopane declined from 2.36 in the fuel oil to 0.36 in the spilled oil. The ratio of ΣC_2 -phenanthrenes/hopane declined from 3.52 in the fuel oil to 0.88 in the spilled oil. Both the C_1 and C_2 -phenanthrenes were below detection in the M1 sediments and can be assumed to have largely been biodegraded. Consequently, although oil spilled from the *Wakashio* in August 2020 is still present within the Mauritius mangrove ecosystem in March 2023, and some components will probably persist for some considerable time especially in anoxic sediment, the vast majority of compounds known to be toxic to aquatic organisms have been lost due to evaporation, dispersion in water, and biodegradation, or are not readily bioavailable. The presence of oil in mangrove sediments has been reported to negatively impact these sensitive ecosystems (Lai and Feng, 1985; Lassalle et al., 2023; Lewis and Pryor, 2013), although the mechanism for this is not fully understood.

A study by Lassalle et al. (2023) utilizing field spectroscopy and drone hyperspectral imaging revealed that continuous exposure of

mangrove trees to high concentrations of oil contamination impacted their long-term health and productivity by imposing permanent stressful conditions. The study also reported that mangrove species differ in their sensitivity to oil, resulting in the more tolerant species obtaining a competitive advantage to recolonize mangrove systems. In a review of the toxicities of oils with regard to their impact on aquatic plants, Lewis and Pryor (2013) reported that mangrove trees are considered more sensitive than aquatic plants associated with the mangrove systems. It can be several years before symptoms are observed and mangrove systems can take as long as 50 years to recover (Lewis and Pryor, 2013). Mangrove seedlings have been found to be more sensitive than mature trees following exposure to oil (Lai and Feng, 1985). It is therefore crucial to know where the spilled oil is present and to have ongoing monitoring of the sites with health checks on the mangroves and their associated plants and animals. Unfortunately, once oil has entered the mangrove system, it would almost certainly cause more harmful effects to attempt to remove it. The current study is very limited in its geographic sampling due to logistical constraints within Mauritius, so the extent of the oil contamination throughout the Mauritius coast is unknown.

3.3. WebGNOME-ADIOS models comparing fate of *Wakashio* fuel oil and traditional marine fuel oils

As with all models, the accuracy of their predictions is largely determined by their quantity and quality of the data used for their training. With regards to the WebGNOME-ADIOS model, there exists many experimental studies and monitoring of real-world spillages of crude oils and fuel oils that can be used to build the models. As VLSFOs are a recent introduction with very limited experimental data (see Sørheim et al., 2020, 2021), the accuracy of the model's output has yet

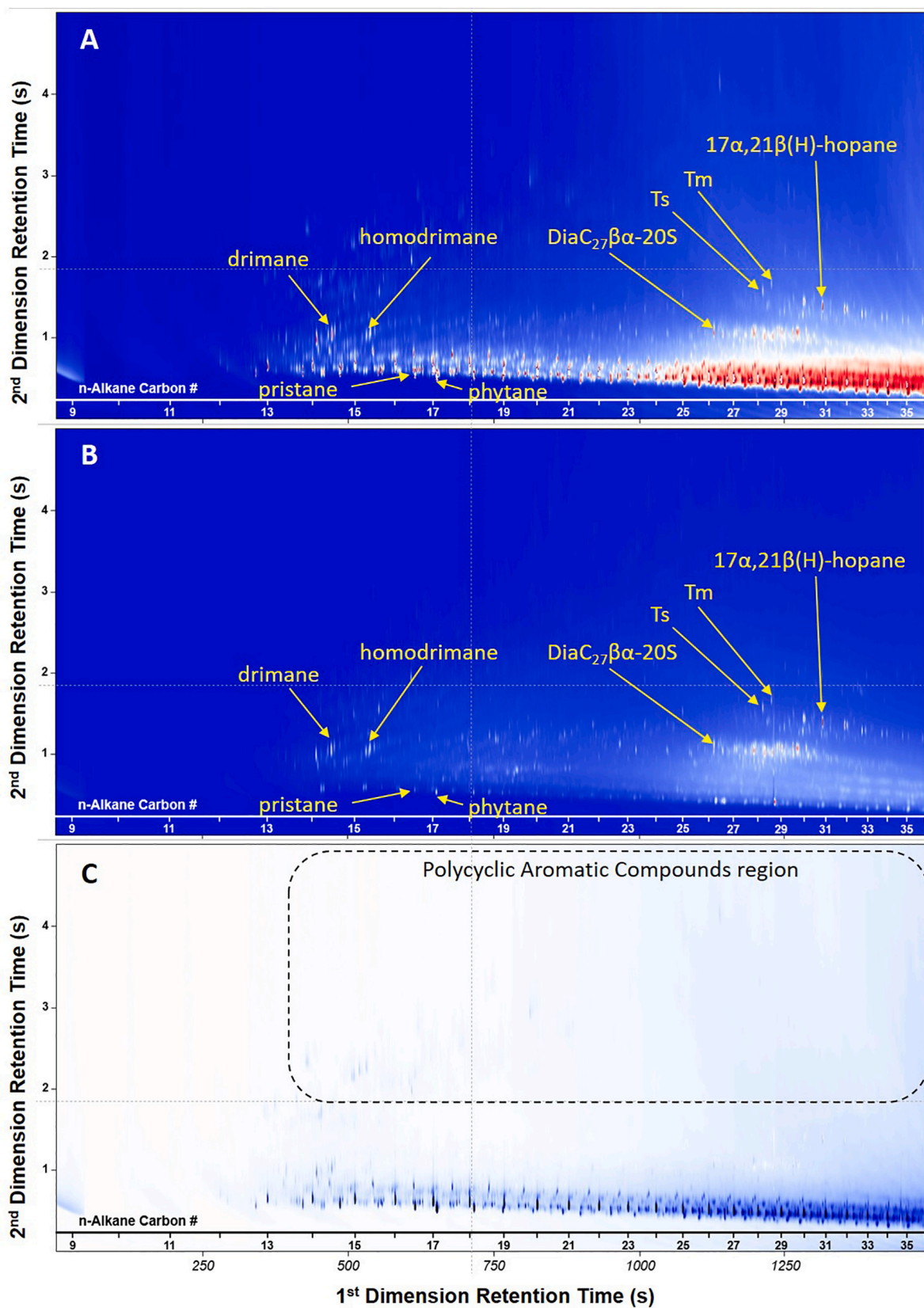


Fig. 4. Comprehensive two-dimensional gas chromatograms of (A) *Wakashio* fuel oil and (B) a sediment sample collected from mangrove site M1 in Mauritius. Peak intensity increases from blue to red. Panel C shows a difference chromatogram in which compounds that are more abundant in the *Wakashio* fuel oil appear blue and those more abundant in the sediment sample appear red. Those that vanish are the same relative abundance in both oils. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

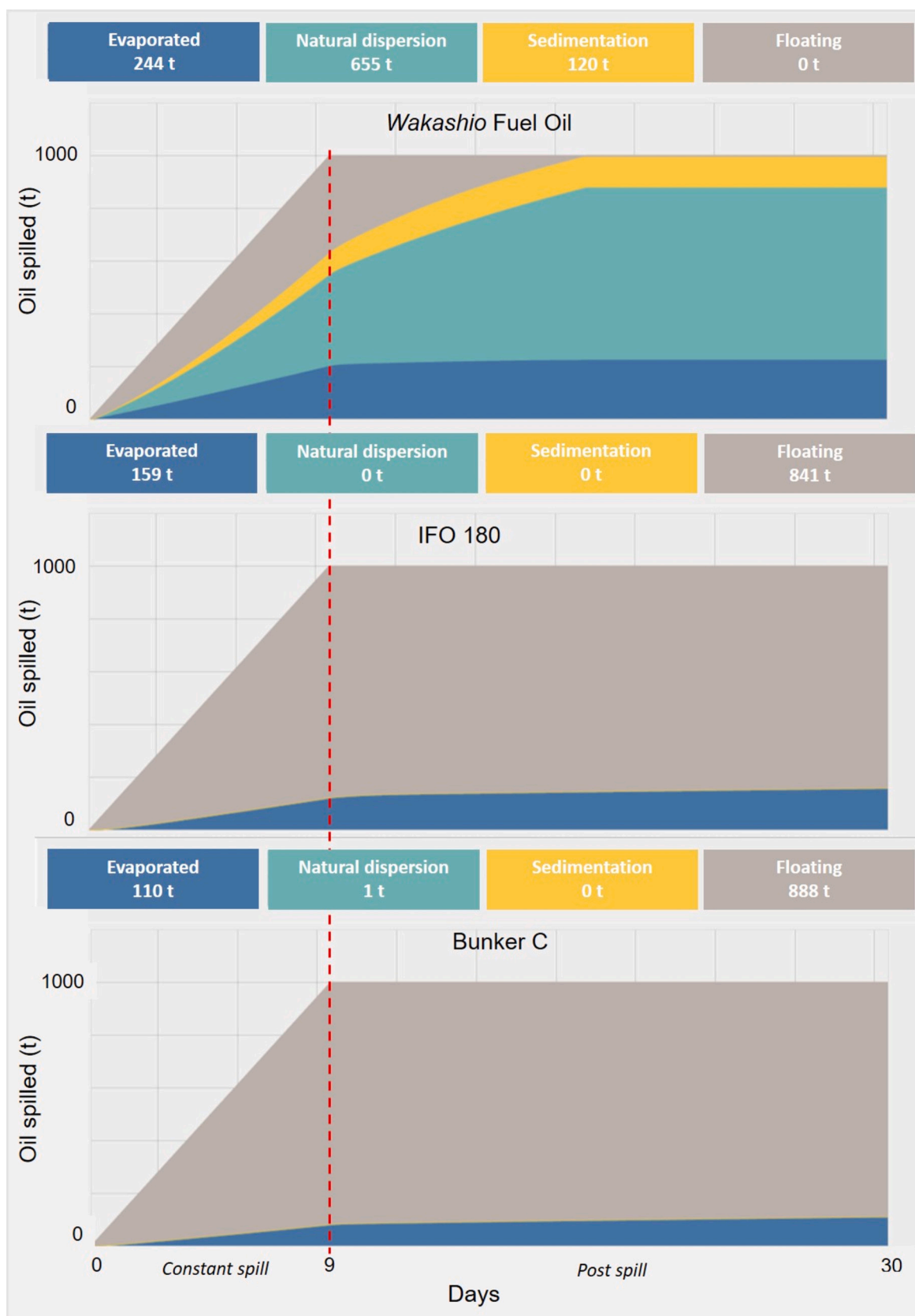


Fig. 5. Oil budgets for *Wakashio* VLSFO (top panel), IFO 180 (middle panel) and Bunker C heavy fuel oil (lower panel) modelled using WebGNOME-ADIOS for an oil spill of 1000 t spilled on the 6th August 2020 under conditions similar to those at the time of the *Wakashio* oil spill. The model assumes a constant spill during the first nine days (red dashed line). The model output shows the total oil in metric tonnes (t) evaporated, naturally dispersed, undergone sedimentation, and remaining floating after 30 days in the environment following commencement of the spill. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

to be tested. The behavior of oil spilled in the sea is largely determined by its API gravity and pour point, in conjunction with environmental factors such as sea temperature and wind speed etc. The *Wakashio* VLSFO (IM-5) has an API of 24.2 which is somewhat lighter than both the Bunker C (API 13.7) and IFO 180 (API 14.8) fuel oils that were used for the ADIOS modeling. The pour point (the lowest temperature at which an oil will flow under standard cooling conditions without stirring) of 9 °C for IM-5 was a little lower than that of both the traditional fuels modelled (15 °C), but in the warm tropical waters of Mauritius of around at 23 °C this parameter should not be such a critical factor as would be the case in much colder seas. Below we discuss the comparative differences in the predicted fate of the three fuel oils and what this may imply in terms of environmental impact.

Comparative models based on the approximate conditions at the time of the *Wakashio* oil spill, suggests that more of the spilled oil would have remained floating for longer if the oil had been traditional marine fuel oils IFO 180 or Bunker C (Fig. 5). Greater quantities of the *Wakashio* fuel oil were modelled to have evaporated, naturally dispersed or sunk to the sea floor than would occur for traditional fuel oils (Fig. 5). This is somewhat of a double-edged sword as it may be possible to recover floating oil if suitable equipment, such as skimmers, are readily available and can be deployed but, if not, the oil is more likely to cause harm to seabirds and other marine creatures, and more likely to come ashore at some later stage. Natural dispersion may lead to some acutely toxic components, such as alkylbenzenes, alkyltetralins and alkyl-naphthalenes, to dissolve and become more bioavailable (Booth et al., 2008; Booth et al., 2007; Donkin et al., 2003; Donkin et al., 1991; Scarlett et al., 2011). On the other hand, dispersion allows for more rapid biodegradation of oil components. Once oil reaches the seabed, it is less likely to biodegrade due to low dissolved oxygen or anoxic conditions but in near shore environments it may be resuspended during storms. Chronic exposure to weathered oil by sediment-dwelling amphipods, *Corophium volutator*, in temperate waters has been shown to cause reduction in growth rate and reproductive success (Scarlett et al., 2007). It is unknown if benthic communities were impacted by the *Wakashio* oil spill but it would be reasonable to assume that sediment-dwelling fauna would have been affected. It is unknown if long-term monitoring of benthic or mangrove communities is in operation in Mauritius.

The viscosities of non-IMO-2020-compliant fuel oils were modelled to reach above 10,000 cSt within hours such that dispersibility would be unlikely (Supplementary Information Fig. S8). For the *Wakashio* fuel oil, it is predicted that dispersibility would rapidly become difficult but not unlikely, remaining well below 10,000 cSt even after a month post spill (Supplementary Information Fig. S8). The average oil (emulsion) density was also predicted to be somewhat lower ($\sim 930 \text{ kg m}^{-3}$) for the VLSFO than that of both the traditional fuel oils ($\sim 1000 \text{ kg m}^{-3}$, Supplementary Information Fig. S9) which would likely remain as oils with entrained water (Fingas and Fieldhouse, 2009).

4. Conclusions

It is regrettable that there has been no reporting of official monitoring of the fate of spilled oil following the grounding of the *Wakashio* in July 2020. The collection of samples and results of analysis of the

spilled oil and sediments has only been possible due to the efforts of volunteers and without any funding from governments or shipping companies. The results of the chemical analysis of sediment samples collected from a mangrove system close to the site of the *Wakashio* grounding clearly show that VLSFO spilled from the ship has contaminated sediments whereupon it has been subject to weathering processes including biodegradation. The relatively low PAC content of the VLSFO spilled from *Wakashio* may have resulted in a reduced impact on organisms due to exposure to soluble toxic hydrocarbons when compared with non-IMO-2020-compliant heavy fuel oils although more of the aromatic compounds in the VLSFO may have been dispersed in the water column. Models comparing the fate of the *Wakashio* VLSFO with that of traditional fuel oils suggested that relatively more of the VLSFO would have evaporated, naturally dispersed or sunk to the benthos than would occur for traditional fuel oils, but how this might have affected the impact upon organisms is difficult to assess. Oil trapped within the mangrove system sediments may be subject to further weathering and biodegradation processes but many recalcitrant components are likely to remain for some time especially under anoxic conditions. There is insufficient data to assess the likely impact of the oiled sediments upon the mangroves and their associated communities. Long-term monitoring of the health of mangrove communities in Mauritius, in association with a comprehensive study of hydrocarbon contamination, would be useful and may be informative with regards to the potential impacts of VLSFO contamination of similar tropical systems.

CRedit authorship contribution statement

Alan G. Scarlett: Writing – review & editing, Writing – original draft, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Robert K. Nelson:** Writing – review & editing, Writing – original draft, Validation, Methodology, Investigation, Conceptualization. **Marthe Monique Gagnon:** Writing – review & editing, Writing – original draft, Conceptualization. **Christopher M. Reddy:** Writing – review & editing, Writing – original draft, Conceptualization. **Kliti Grice:** Writing – review & editing, Writing – original draft, Resources, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

Peter Hopper (CU) is thanked for technical support. This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors. CMR and RKN were supported by the National Science Foundation (OCE-1634478 and OCE-1756242). GC×GC analysis support provided by WHOI's Investment in Science Fund. We thank the anonymous citizens in Mauritius for sample collection. We also thank the anonymous reviewers for their comments and suggestions that has helped improve this manuscript.

Appendix A

Appendix 1

Names and abbreviations of compounds identified in saturated hydrocarbon fractions of oil and of sediment samples.

Abbreviation	Compound name	Mass (Da)
C23TriT	Tricyclic terpenoid (C ₂₃ H ₄₂)	318
C24TriT	Tricyclic terpenoid (C ₂₄ H ₄₄)	332
Ts	18 α (H)-22,29,30-trisnorhopane (C ₂₇ H ₄₆)	370
Tm	17 α (H)-22,29,30-trisnorhopane (C ₂₇ H ₄₆)	370
BNH	17 α (H),21 β (H)-28,30-bisnorhopane (C ₂₈ H ₄₈)	384
NH	17 α (H),21 β (H)-30-norhopane (C ₂₉ H ₅₀)	398
C29-Ts	18 α (H),21 β (H)-30-norhopane (C ₂₉ H ₅₀)	398
NM	17 β (H),21 α (H)-30-norhopane (C ₂₉ H ₅₀) normoretane	398
H	17 α (H),21 β (H)-hopane (C ₃₀ H ₅₂)	412
M	17 β (H),21 α (H)-hopane (C ₃₀ H ₅₂) moretane	412
HH (S)	17 α (H),21 β (H)-22S-homohopane (C ₃₁ H ₅₄)	426
HH (R)	17 α (H),21 β (H)-22R-homohopane (C ₃₁ H ₅₄)	426
2HH (S)	17 α (H),21 β (H)-22S-bishomohopane (C ₃₂ H ₅₆)	440
2HH (R)	17 α (H),21 β (H)-22R-bishomohopane (C ₃₂ H ₅₆)	440
3HH (S)	17 α (H),21 β (H)-22S-trishomohopane (C ₃₃ H ₅₈)	454
3HH (R)	17 α (H),21 β (H)-22R-trishomohopane (C ₃₃ H ₅₈)	454
4HH (S)	17 α (H),21 β (H)-22S-tetrakishomohopane (C ₃₄ H ₆₀)	468
4HH (R)	17 α (H),21 β (H)-22R-tetrakishomohopane (C ₃₄ H ₆₀)	468
5HH (S)	17 α (H),21 β (H)-22S-pentakishomohopane (C ₃₅ H ₆₂)	482
5HH (R)	17 α (H),21 β (H)-22R-pentakishomohopane (C ₃₅ H ₆₂)	482

Appendix B. Supplementary data

Supplementary Information contains a map showing sample collection locations, GC–MS chromatogram of sediment uncontaminated by oil from the *Wakashio*, GC×GC-FID chromatograms comparing replicates of sediment extracts and those of the *Wakashio* fuel oil and previously analyzed field sample, modelled oil viscosities and densities. Supplementary data to this article can be found online at doi: <https://doi.org/10.1016/j.marpolbul.2024.117283>.

Data availability

Data will be made available on request.

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