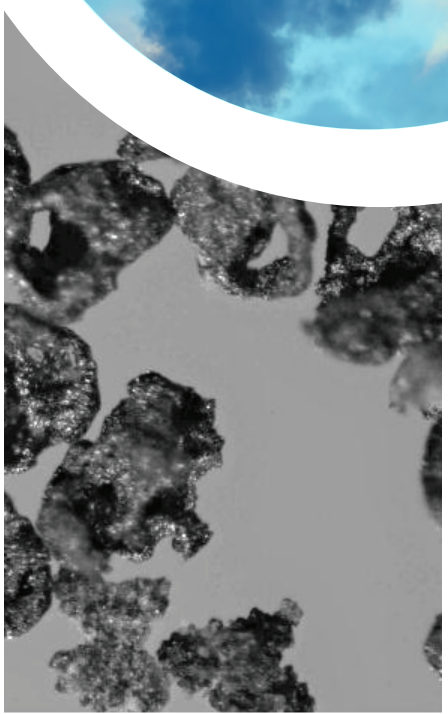
Greenpeace Research Laboratories
Analytical Results

Analysis of settled dust particles from the city of Kenitra, Morocco



GREENPEACE
غرينبيـــــــس

جمعية أوكسجين للبيئة والصحة
Oxygen Association for Environment and Health

Disclaimer:

The findings in this report cannot conclusively identify the precise source of the black dust. It should be noted that the reference to any facility or activity in this report is made solely within the context of scientific observation and environmental assessment, particularly in relation to its proximity to the sampling locations. Such references should not be interpreted as an allegation, attribution of responsibility, or identification of any facility as a source of pollution.

The proximity of the sampling sites to a power plant, which is known to operate periodically and reportedly uses heavy fuel oil, represents a relevant observational factor that may warrant further investigation. However, definitive source attribution would require additional targeted investigations, source-specific analyses, and supporting evidence beyond the scope of the present study.

Introduction

Two samples of settled black dust, reported to have been collected on 15-16th August 2022 from the city of Kenitra in Morocco, were received by Greenpeace Laboratories for analysis on 30th August 2022. The samples were collected in areas close to a power station located in a nearby industrial area. Locals report that the power station uses heavy fuel oil for fuel. Both samples consisted of dry fine black powder or dust, which had been collected and stored in new, clean plastic zip lock bags, and were delivered to the laboratories in these containers. On receipt, the samples were stored in the dark at 4 Celsius until analysis. Details of the samples received are provided in Table 1

Table 1

GRL sample code	Sampling date,time	Sampling location	GPS	Distance (km) & direction from power station
MA22001	15-8-2022 , 6.30 pm	Roof of a house, Bakers market, Kenitra	34.26428 N, -6.56489 W	2.3 Km, south
MA22002	16-8-2022 , 7.15 pm	Roof of a house, Bab Fez, Kenitra	34.27249 N, -6.55728 W	1.5 Km, south-southeast

Table 1: details of samples received and analysed at the Greenpeace Research Laboratories

Greenpeace Research Laboratories
School of Biosciences
Innovation Centre Phase 2
Rennes Drive
University of Exeter
Exeter EX4 4RN, UK

CONTENT

Materials & Methods

Each sample was sieved through various sized meshes to determine the range of particle sizes within the material. For each sample, the predominant size fractions, with particle sizes between 63 µm and 250 µm, was used for the following range of forensic analytical techniques:

Visual microscopy

Quantitative analysis for metals using ICP-MS following acid digest

Qualitative GC-MS screening for solvent-extractable semi-volatile organic contaminants (sVOCs)

Qualitative pyrolysis GC-MS for semi-volatile organic compounds and products of pyrolysis

Total carbon analysis

Fourier Transform Infrared (FT-IR) analysis

Further details of the methods for each type of analysis are set out in Annex 1.

Results

The following sections provide the results obtained from each of the analyses outline above.

Particle size distribution

For the two samples, the majority (94-95 %) of particles were below 355 µm, the remainder being predominantly composed of larger particles that were visually different to the black particles that made up the bulk of each sample. Of the fraction with particles below 355 µm, the majority was between 63 µm and 250 µm (see Table 2 for details). The visual microscopy images of the fraction between 250 µm and 355 µm indicated particles that were visually very similar to those in the 63-250 µm fraction (see images below). For both samples, the small quantity of particles below 63 µm was light brown in appearance, visually different to the main fraction.The range of particle sizes in the samples is consistent with fly ash generated by power stations using heavy fuel oil, especially under poor combustion conditions (Al-Degs et al. 2014, Kwon et al. 2004, Yu et al. 1996), though particles from other sources could also have similar size ranges.

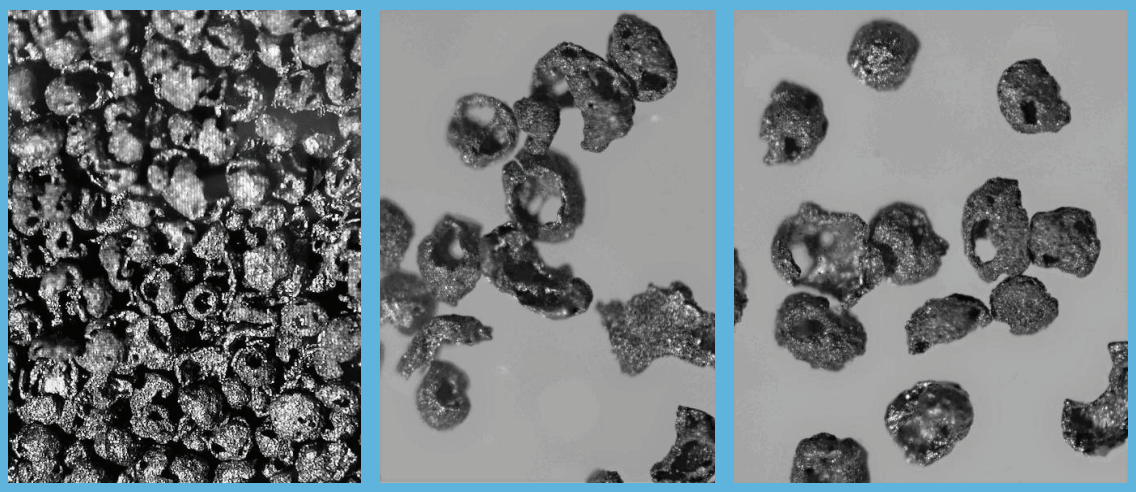
Size fraction	MA22001	MA22002
355 - 250 µm	24.5 %	34.1 %
63 - 250 µm	74.4 %	65.6 %
<63 µm	1.1 %	0.3 %

Table 2: Mass percentages for various size fractions of the material that passed through the 355 µm mesh

Visual microscopy

Observation of particles in the 63-250 µm fraction of both samples using a visual microscope indicated that the material is composed of hollow cenosphere particles **(Figure 1).** These types of structures are commonly found in fly ashes, including fly ash from heavy fuel oil combustion (Caramuscio et al. 2003).

(a).



(b).

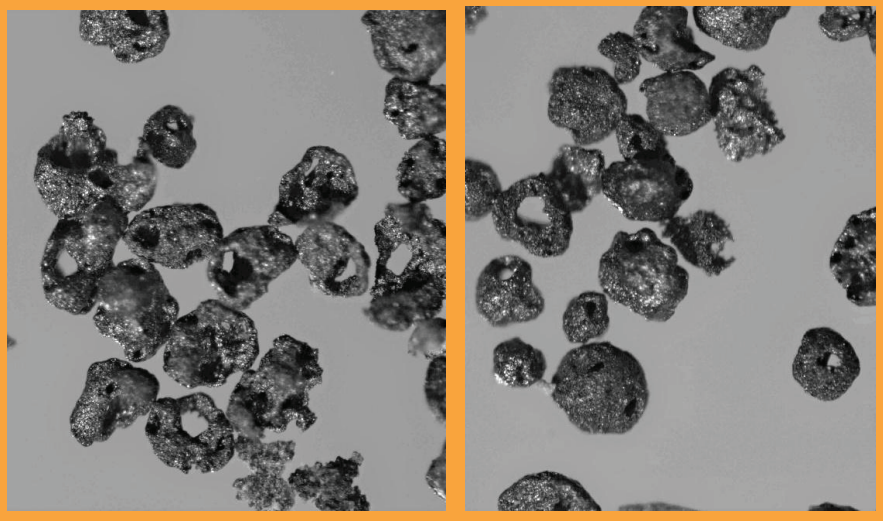


Figure 1: Visual microscopy images of 63-250 µm fraction for **(a) MA22001** and **(b) MA22002**

Particles in the 250-355 µm fraction of both samples had a similar morphology to those in the 63-250 µm fraction **(Figure 2).**

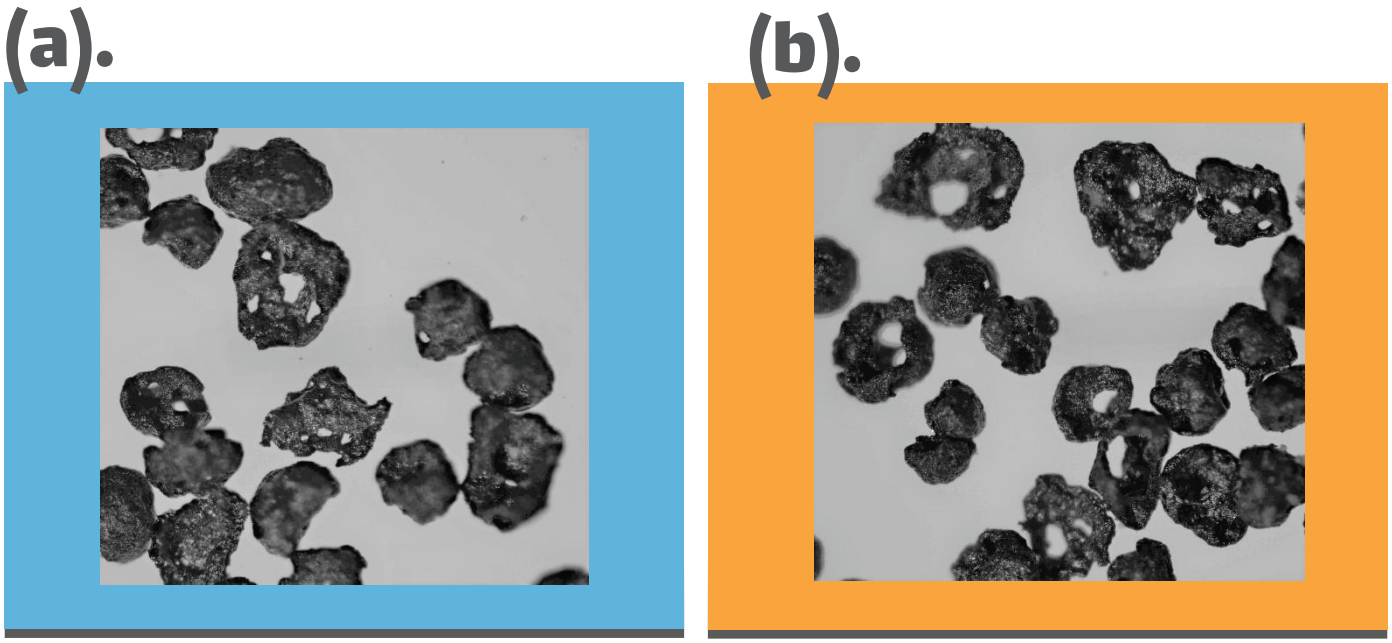


Figure 2: Visual microscopy images of 250-355 µm fraction for (a) MA22001 and (b) MA22002

Quantitative analysis for metals using ICP-MS

The samples contained notable concentrations of vanadium (1640-3060 mg/kg) and nickel (656-1180 mg/kg). Fly ash from heavy fuel oil have been reported to contain relatively high concentrations of vanadium and nickel, though typically at concentrations even higher than those in the 2 samples, ranging from 7000-61000 mg/kg vanadium and 2000-14000 mg/kg nickel. In comparison, coal fly ashes typically have lower concentration of these metals, in the range 100-200 mg/kg for vanadium and 30-200 mg/kg for nickel (Al-Degs et al. 2014). The two samples also contained other metals and metalloids at concentrations lower than those commonly found in coal fly ash, including arsenic, boron and uranium (EPRI 2009)

Qualitative GC-MS screening for sVOCs

No solvent extractable organic compounds were identified in either sample.

Qualitative pyrolysis GC-MS for sVOCs and products of pyrolysis

No semi-volatile organic compounds could be detected after heating either sample to 200°C, suggesting that the material in both cases is relatively inert and inorganic in nature.

Metal/metalloid		MA22001	MA22002
Aluminium	Al	2800	5380
Antimony	Sb	0.6	1.9
Arsenic	As	2.7	4.3
Barium	Ba	30.8	114
Beryllium	Be	0.10	0.21
Boron	B	15	23
Cadmium	Cd	0.28	0.28
Calcium	Ca	2790	3040
Cerium	Ce	8.9	8.9
Chromium	Cr	44.3	38.5
Cobalt	Co	6.08	10.4
Copper	Cu	34.6	41.8
Gallium	Ga	1.89	4.77
Iron	Fe	3660	9580
Lead	Pb	18.1	39.4
Magnesium	Mg	1500	1850
Manganese	Mn	84.4	120
Mercury	Hg	<0.1	<0.1
Molybdenum	Mo	24.0	42.4
Nickel	**Ni**	**656**	**1180**
Potassium	K	1540	1740
Selenium	Se	0.30	0.52
Sodium	Na	2020	1610
Strontium	Sr	33.7	34.0
Thorium	Th	0.44	0.86
Tin	Sn	0.71	6.09
Titanium	Ti	19	127
Uranium	U	0.20	0.25
Vanadium	**V**	**1640**	**3060**
Zink	Zn	180	222

Table 3:
Concentrations of metals and metalloids (mg/kg dry weight) for the 63-250 µm size fractions

Pyrolysis at 700°C yielded only minor peaks from products of pyrolysis **(Figure 3),** in greater number and abundance in sample MA22001 than in MA22002, but again consistent with the material being relatively inert. Those pyrolysis products that were detected included minor residues of benzene & toluene, and of derivatives of furan and phenols, which are common products of pyrolysis of many organic materials and are not diagnostic of any particular source. Also evident, especially in sample MA22001, were residues of derivatives of furanone and furfural, which may be more indicative of the presence of small quantities of biogenic material in the sample (e.g. small fragments of plant matter or soil dust) than being of fossil carbon origin in themselves. Although care was taken only to include the black particles in the sub-samples subjected to pyrolysis, it was not possibly to ensure the exclusion of all other matter that may have been deposited (and therefore subsequently collected) along with the black particles, so it is possible that the minor pyrolysis products identified arose from other associated materials mixed with the spheres.

The inert nature of the black particles in the 63-250 µm fraction was further evidenced by microscopic observation of the sub-samples after pyrolysis, in which they appeared physically unchanged despite the intense heating to 700°C for 15 seconds **(Figure 4).** This result is consistent with previous reports for heavy oil fly ash particles, which also appeared largely unchanged following pyrolysis at 900°C (Caramuscio et al. 2003).

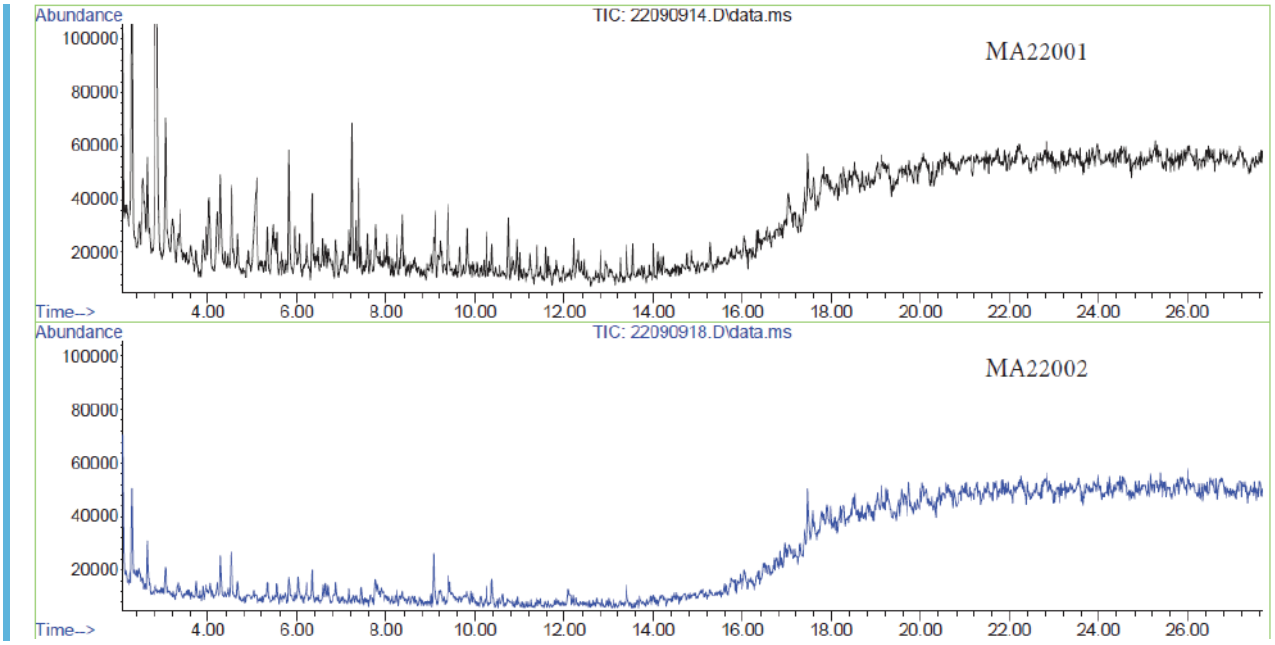


Figure 3: Pyrograms (total ion chromatograms from pyrolysis GC-MS) for sub-samples of the 63-250 µm fractions for MA22001 and MA22002, showing only minor peaks above the baseline.

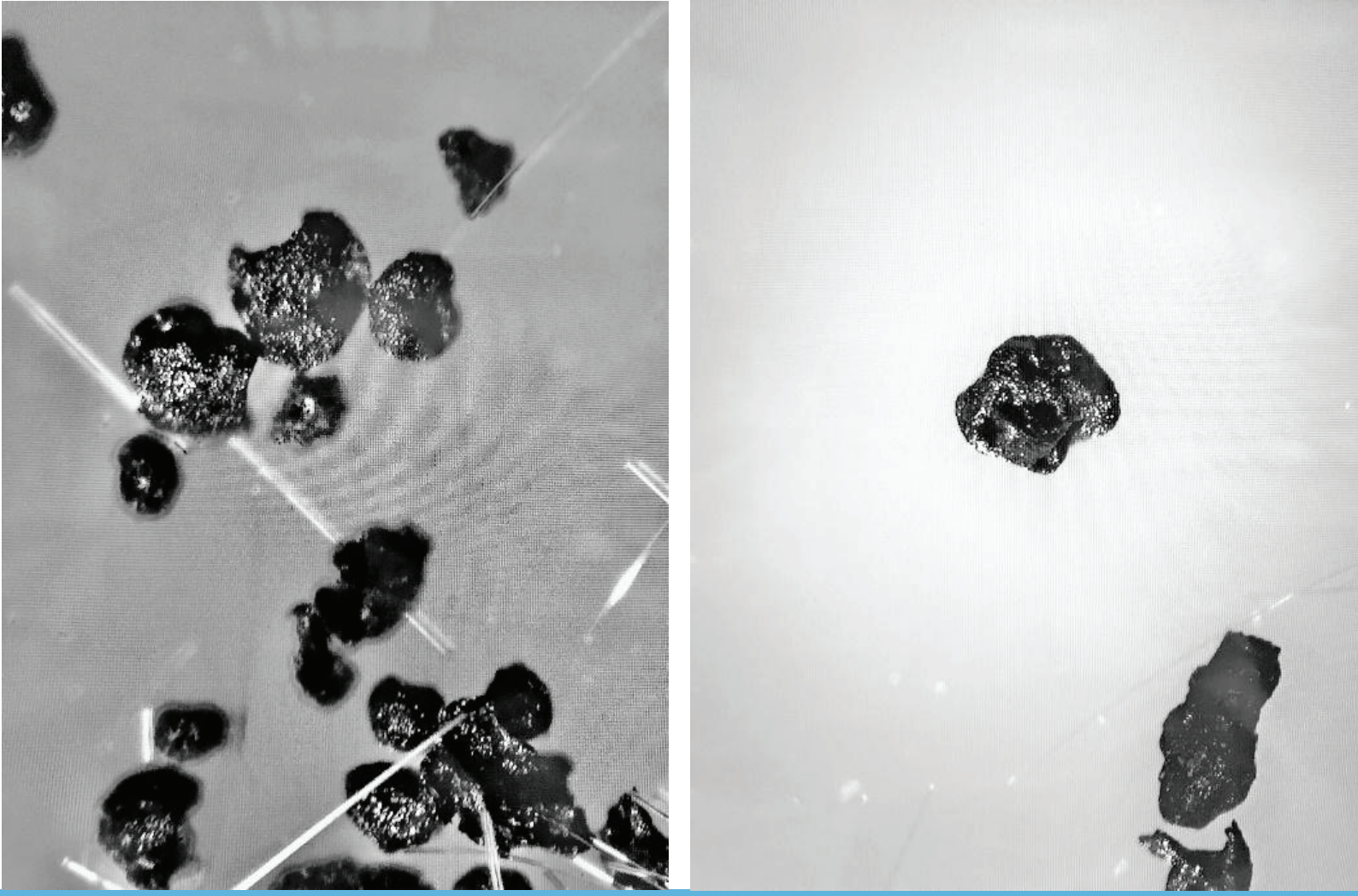


Figure 4: Visual microscopy images of 63-250 µm fraction following pyrolysis. Fibres visible in the left-hand image are from the quartz wool used to hold the sample in position in the pyrolysis tubes during analysis

For qualitative comparative purposes only, equivalent quantities of two certified reference materials (fly ash and pulverised fuel ash) were also subject to the same pyrolysis GC-MS analysis, along with a sample of coal dust (dust fragments in the same size fraction prepared from domestic heating coal purchased in the UK) of a similar quantity and size fraction in order to exclude the possibility that the black dust collecting on the rooftops was related to the handling of uncombusted coal, given the visual similarity of the materials by eye.

Pyrograms (chromatograms from qualitative pyrolysis GC-MS analysis) for the two fly ash samples are shown in comparison to those from the two rooftop dusts MA22001 and MA22002 in figure 5 below. Although this sort of comparison is purely illustrative in nature, as corresponding peaks at any particular retention time (horizontal axis) do not necessarily represent the same chemicals (see below),

the comparison does serve to indicate that samples of fly ash can also similarly yield some minor products of pyrolysis, despite their origin as waste from a high temperature combustion process. In addition, many of the chemicals yielded through pyrolysis of the ashes were indeed similar to those yielded by pyrolysis of the two black dust samples, including benzene, toluene, furan, phenol and their derivatives.

By contrast, and again for qualitative comparative purposes only, the pyrogram from the pyrolysis of an equivalent quantity of coal dust was markedly different **(see Figure 6).** This simply provides an illustration of the type of pyrogram that might be expected if the black dust was a material with a significant content of combustible organic carbon.

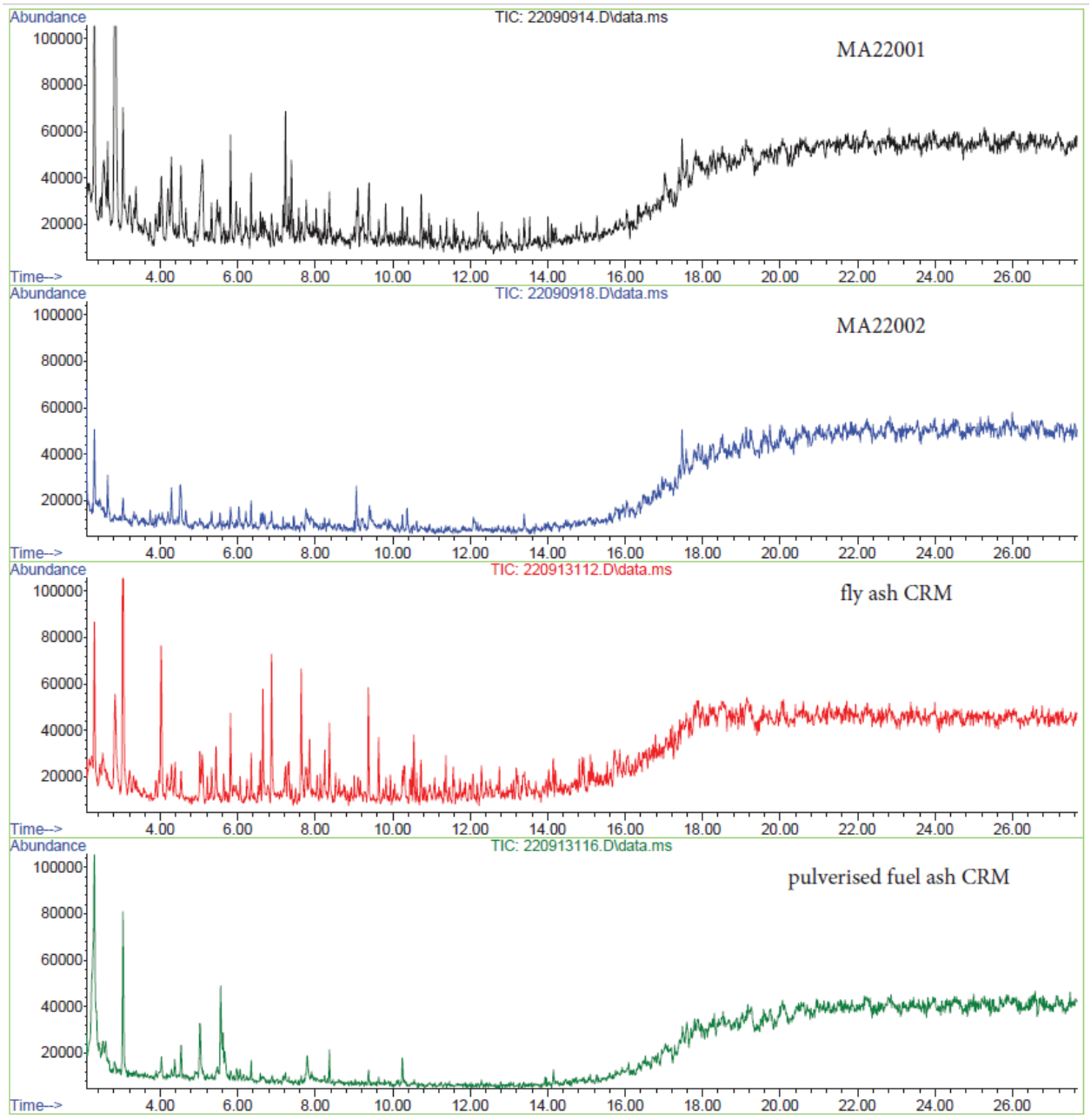


Figure 5: Pyrograms (total ion chromatograms from pyrolysis GC-MS) for sub-samples of the 63-250 µm fractions for MA22001 and MA22002, compared to those for two fly ash certified reference materials (CRMs)

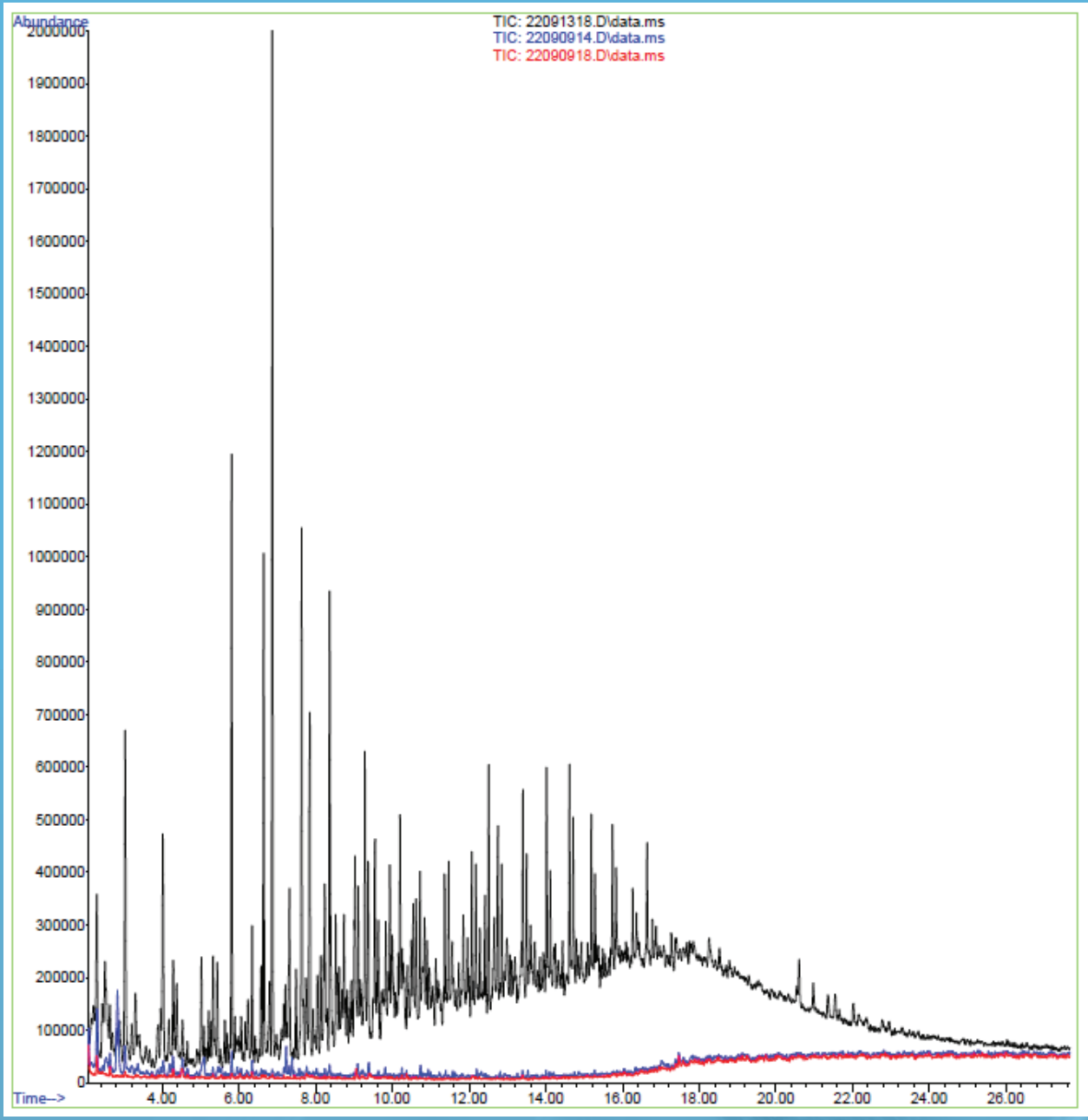


Figure 6: Pyrograms (total ion chromatograms from pyrolysis GC-MS) for sub-samples of the 63-250 µm fractions for MA22001 and MA22002 (blue and red lines), compared to those for an equivalent mass of domestic heating coal fragments in the same size fraction (black line).

Total carbon analysis

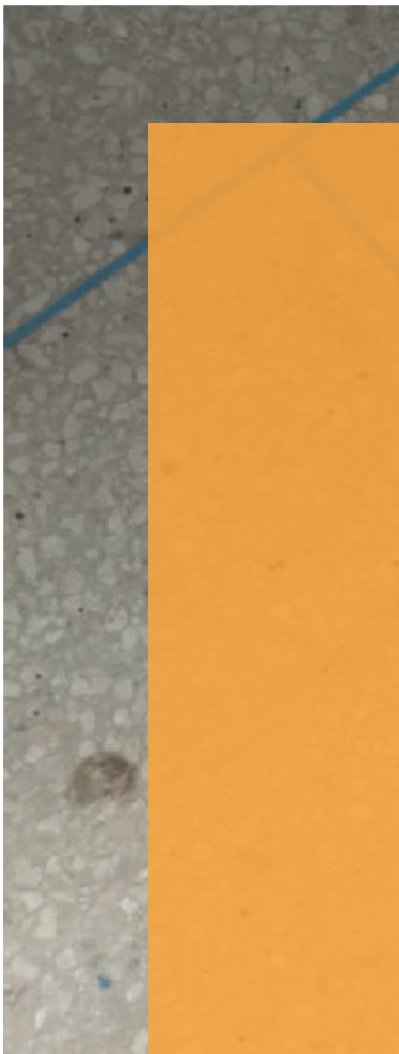
The concentration of total carbon in the two samples is given in Table 4. The concentrations in these samples are consistent with reported concentrations of total carbon in heavy oil fly ash (Caramuscio et al. 2003, Kwon et al. 2004)

Sample	Total carbon (%)
MA22001	54.6
MA22002	68.1

Table 4: Concentration of total carbon (mass %) for the 63-250 µm size raction of each sample

FTIR

Despite numerous attempts, it was not possible to retrieve a meaningful FT-IR spectrum from a thin layer of the ground material on the ATR crystal, most likely because of a combination of its very dark colour and its largely inorganic nature. Alternative techniques such as x-ray microanalysis would likely be necessary in order to obtain information on the elemental composition and likely structure.



Concluding remarks

Two samples of settled black dust collected from rooftops in the city of Kenitra, Morocco, were characterised as far as possible using a range of environmental forensics analytical techniques. Visual microscopy confirmed that the material consisted mainly of dark-coloured hollow spheres, primarily in the size fraction 63- 250 µm and morphologically similar to cenospheres found as a component of fly ashes generated by thermal combustion processes.

Material in the predominant size fraction showed a high carbon content, but was found to contain no readily extractable organic carbon components and yielded only minor products of pyrolysis at 700°C, suggesting that the carbon content was largely inorganic in nature. The spheres were morphologically unaltered during pyrolysis, appearing identical before and after heating to 700°C for 15 seconds.

In terms of metals and metalloids, only levels of vanadium and nickel were notably elevated. Taken together, all these lines of evidence are consistent with the characteristics of fly ashes generated through the combustion of heavy fuel oil, especially under sub-optimal combustion conditions.

It is not possible from these analyses to confirm the specific origins of the black dust in terms of point sources. However, given the known proximity of the sampling locations to a power plant that operates periodically and reportedly burns heavy fuel oil, the potential for this facility to have been the source of the black dust deposited on the rooftops clearly deserves more detailed and urgent investigation.

Furthermore, although the results of this study suggest that the material that we received for analysis was relatively inert in nature, and did not contain significant levels of toxic contaminants, it is important to keep in mind that the dust that had settled in those locations was of a relatively large size fraction, such that what was collected and subjected to analysis may only represent one part of the total particulate and chemical loading arising from the source. In other words, the deposition of the very visible black dust analysed in this study may be just one symptom of a broader problem of emissions to air across all size fractions, this dust showing characteristics consistent with emissions of fly ash from a large combustion source but not in itself representing the totality of those emissions. More comprehensive sampling of airborne contaminants in the region, perhaps in combination with modelling of emission plumes from known point sources, would be necessary in order to investigate air pollution in the area more comprehensively and to determine implications for the health of residents of Kenitra.

For more information please contact:
Kevin Brigden, Beatriz Callejo, or David Santillo

References

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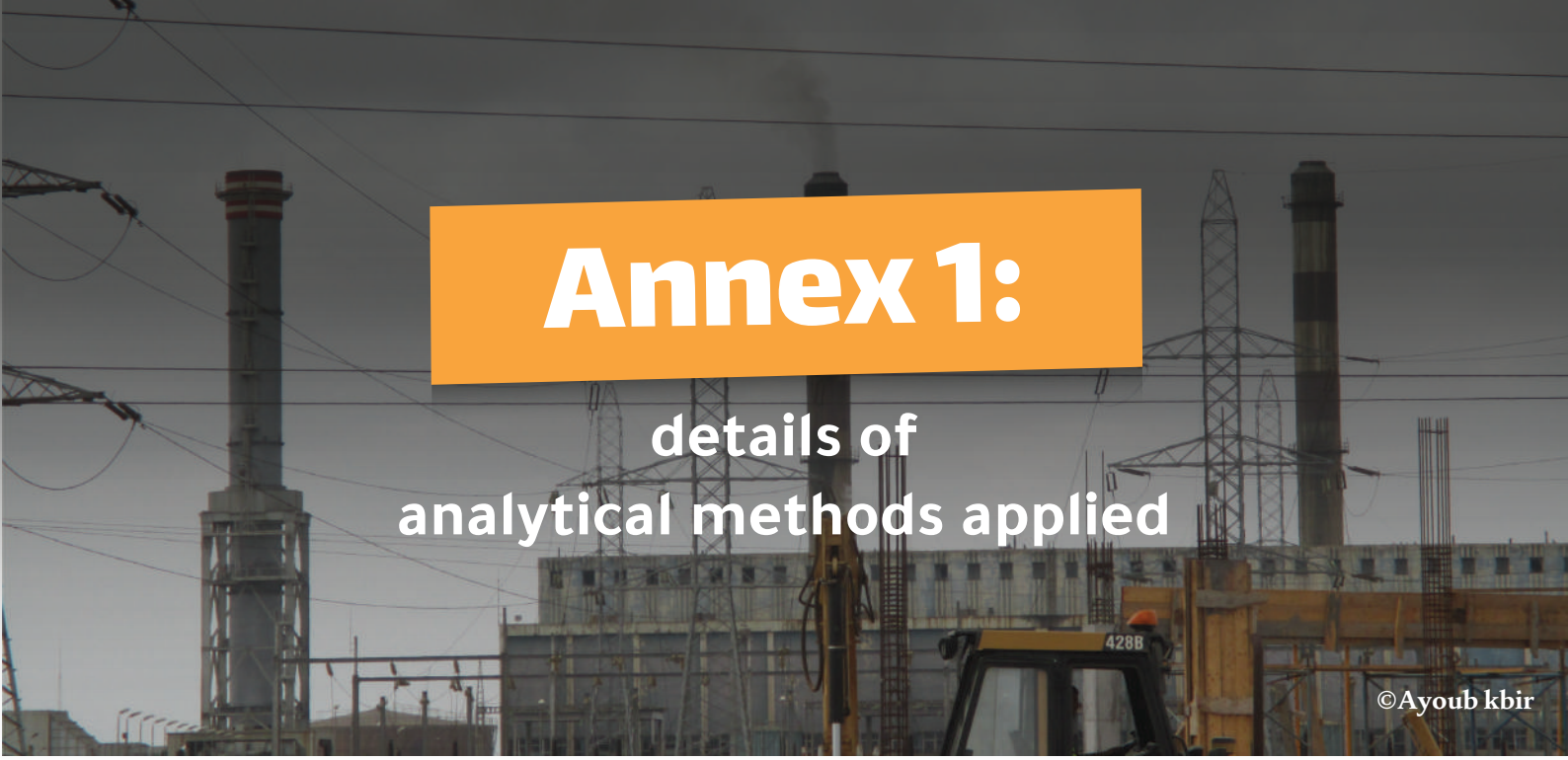

Annex 1:

details of analytical methods applied

Metals

For each sample, the size fraction between 250 µm and 63 µm was used for metals analysis. Approximately 0.2 g of the sample was accurately weighed and digested with 5.0 ml concentrated nitric acid and 0.5 ml concentrated hydrochloric acid, firstly overnight at room temperature then using microwave-assisted digestion with a CEM MARS Xpress system with temperature ramping: heating to 200 °C over 20 minutes and held at 200 °C for 20 minutes. Following cooling, each digest solution was filtered and made up to 25 ml with deionised water. Prior to analysis, each digest solution was diluted 1:4 using deionised water.

One sample was prepared for ICP analysis in duplicate and analysed to verify method reproducibility. A blank sample was also prepared with the samples, together with two certified reference materials; LGC6180, pulverised fuel ash from coal-based power station certified by the Laboratory of the Government Chemist, UK, and BCR-038, fly ash from Pulverised coal certified by the Commission of the European Communities

Sample digests were analysed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) using an Agilent 7900 Spectrometer utilising a collision cell with helium as the collision gas to minimise polyatomic interferences. Multi-element standards, matrix matched to the samples, at concentrations of 1, 10, 100 and 1000 µg/l respectively, other than for mercury (1, 2, 5, 20 µg/l respectively) were used for instrument calibration.

Calibration was validated by the analysis of quality control standards at 80 µg/l and 800 µg/l (4 µg/l and 16 µg/l for mercury) prepared in an identical manner but from different reagent stocks to the instrument calibration standards. Analysis employed in-line addition of an internal standard mix at 100 µg/l (Scandium, Germanium, Yttrium, Indium and Terbium). Any sample exceeding the calibration range was diluted accordingly, in duplicate, and re-analysed.

Semi-volatile organics (sVOCs) using solid phase extraction (SPE) and liquid injection GC-MS

Sample extraction

Approximately 0.5g of each sample was sub-sampled into a suitable glass container and 10µg of deuterated Naphthalene (Internal Standard) was added, followed by 5mL of Pentane:Toluene (95:5). A procedural blank, consisting of 5mL of Pentane:Toluene (95:5) was also prepared.

Samples and blank were then sonicated in a water bath at 30°C for 30 minutes. All samples were then submitted to a florisil cleaning procedure: glass cartridges were assembled with a pre-cleaned filter and 2g of florisil, followed by a final filter, and conditioned with 5mL of Pentane.

All extracts were collected into suitable glass containers. 1 mL of each sample was then transferred into 2mL autosampler vials and analysed using liquid injection GC/MS

GC/MS analysis

For the total organic compounds screening, samples were analysed using an Agilent 6890 Series II GC with Restek Rtx-17Sil column (30m, 0.25mm ID, 0.25 µm film thickness) linked to an Agilent 5975B Inert MSD operated in EI mode and interfaced with an Agilent Enhanced Chemstation data system.

Total Ion chromatograms (TIC) and Selected Ion Monitoring (SIM) chromatograms were obtained. The GC oven temperature program employed was as follows: an initial temperature of 40°C, raised to 260°C at 10°C/min, then to 295°C at 50°C/min (held for 10 min), then to 325°C at 50°C /min (held for 25 min), finally raised to 330°C at 50°C/min (held for 1 min). The carrier gas was helium, supplied at 1ml/min.

Identification of compounds was carried out by matching spectra obtained during analysis against both the Wiley W10N11 and Pesticides Libraries, and against spectra obtained for certain target compounds, applying expert judgment to verify the quality of the mass spectral match for each peak in turn in order to avoid misidentifications.

Pyrolysis GC-MS

Two sub-samples of approximately 500 µg of homogenised material from the same size fraction (consisting of between 30 and 40 of the individual spheres in each case) were transferred to separate quartz pyrolysis tubes, which had been pre-cleaned by pyrolysis at 7000C for 15 seconds. Samples were held in place in the tubes using a thin plug of quartz wool, which had also been pre-pyrolysed. Samples were then subjected to qualitative double-shot pyrolysis GC-MS using a CDS Pyroprobe 6200 pyrolyser, equipped with a CDS 6250T DISC Autosampler carousel and interfaced with an Agilent 6890 GC and 5973 MSD.

Each sample was first heated in the pyrolysis sample chamber to 200°C at a rate of 20°C/ms, and the temperature held for 15s. The chamber was swept with helium carrier gas and any semi-volatile compounds emitted from the sample were directed initially to a cold trap held at 50°C, which was then ramped to 280°C for a period of 3 minutes in order to desorb those compounds onto the GC column for GC-MS analysis. Each sample was then heated a second time, this time to 700°C at a rate of 20°C /ms and again held for 15 seconds, with the products of pyrolysis being directed to the trap, and the trap then desorbed in the same way to the GC-MS.

The GC column used was a 30m Restek Rxi-17Sil MS, internal diameter 0.25mm, film thickness 0.25 µm, with a constant flow rate of helium carrier gas of 1 ml/min. The oven was held at an initial temperature of 50°C for 1 minute, before ramping at 15°C /min to a final temperature of 300°C, which was held for 10 minutes, giving a total run time of 27.67 minutes.

Identification of compounds was carried out by matching spectra obtained during analysis against both the Wiley 12 and NIST 20 Libraries, applying expert judgment to verify the quality of the mass spectral match for each peak in turn in order to avoid misidentifications.

Total Carbon analysis

Approximately 5 mg of each samples was weighed into 8 by 5 mm tin capsules using a Sartorius (Model MC5, Sartorius AG, Germany) microbalance. These samples were analysed using a Flash 2000 Elemental Analyser (ThermoFisher Scientific, Netherlands), using EDTA as a standard. A calibration curve using a K-factor fitting was applied before the samples were run and an additional standard was run at the end of the samples to check analysis accuracy.

Fourier Transform Infrared (FT-IR) analysis

Subsamples of approximately 100mg of ground material from each sample was analysed using Attenuated Total Reflection (ATR) Fourier Transform Infrared (FT-IR) spectroscopy, using a PerkinElmer Frontier spectrometer. FT-IR spectra (mid-infrared) were obtained for each sample by scanning in the wave number range between 4000 and 650 cm-1, at a resolution of 4 cm-1, and acquiring 4 scans per sample. All spectra obtained were processed using PerkinElmer's Spectrum software (version 10.5.4), enabling post-acquisition background subtraction and normalisation of the data and subsequent comparison against a number of commercially available spectral databases.

About Greenpeace MENA:

Greenpeace MENA is a non profit completely independent - politically and financially organization. Established in 2018, we are one of the newest offices of the Greenpeace global network that consists of 27 independent national and regional organizations in over 55 countries as well as its co-ordinating body, Greenpeace International. The MENA region is our home. We work creatively and collaboratively to reduce the environmental, economic, and social impacts of climate disasters and push local and innovative solutions, empowering our communities to flourish and live in harmony with their environment.

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The samples were provided by the president of the Oxygen Association for Environment and Health in Kenitra, Morocco, Ayoub Krir, Researcher in Spatial Planning and Sustainable Development.

Oxygen Association for Environment and Health - Morocco

Contact informations

Youtube

LinkedIn

+212 (0) 7 08 87 88 03

Facebook

tiktok

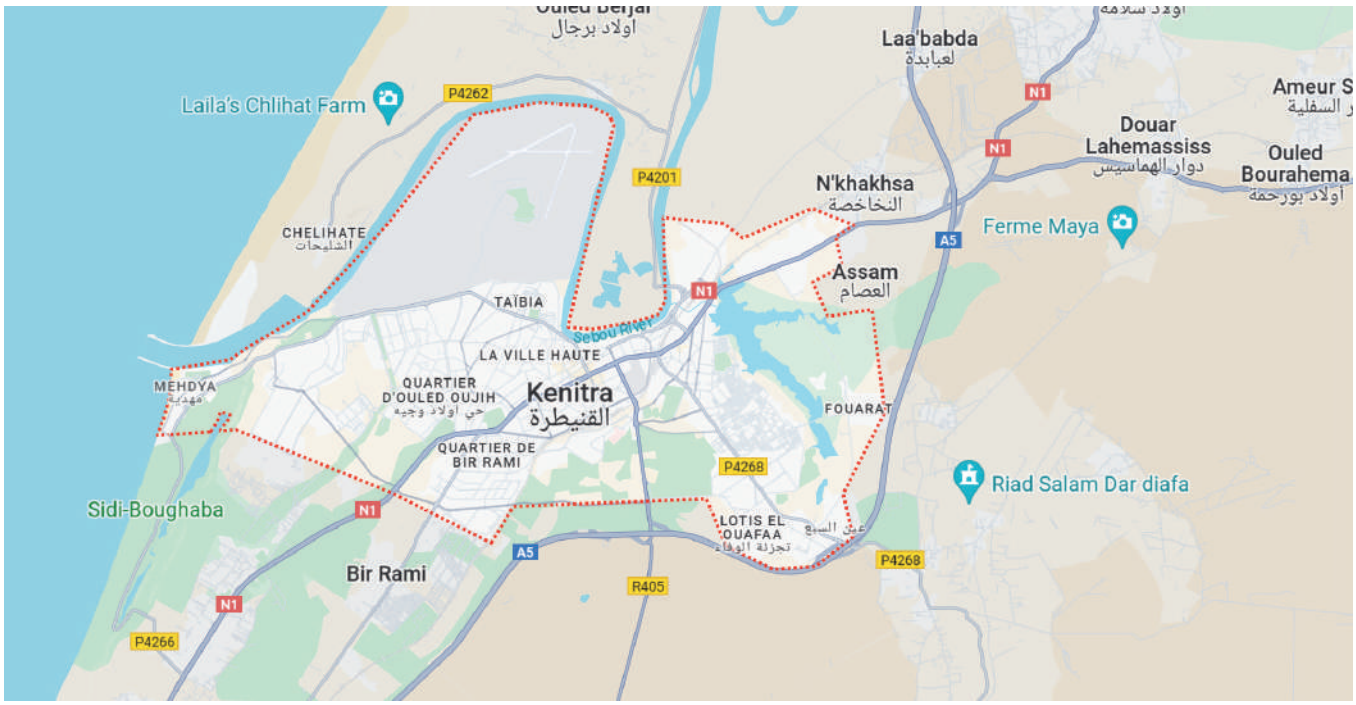
oxygeneass@gmail.com

Instagram

Twitter

Threads

+212 (0) 6 18 73 46 39



KENITRA - MOROCCO

صوت غرينبيس

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