Measurement of fugitive emissions during harbour operations

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Abstract

Fugitive emissions pose problems both for general air quality management as well as for the operational management of the facilities. In harbours, activities such loading, unloading and transport of dusty materials are important sources of particles fugitive emissions. Therefore, there is a growing concern about air quality in these areas as a result of the high impact of the operations on human health and environment.

The aim of this study was to estimate the impact of harbour activities on Air Particulate Matter (APM) levels and composition. This work was based on experimental campaigns carried out in a Portuguese harbour when three types of bulk materials – fertilizer, phosphorite from Syria and phosphorite from Morocco - were handled. High time resolution monitors were installed close to the unloaded area and recorded APM concentrations and meteorological variables. $PM_{2.5}$ and $PM_{2.5-10}$ were also collected during unloading operations, in polycarbonate filters by Gent samplers. A complete chemical characterization of collected samples was made by the techniques Instrumental Neutron Activation Analysis and Particle Induced X-Ray Emission.

Results showed that manipulation of materials during harbour operations resulted in high emissions of particles, especially from the coarse fraction. These emissions were very affected by the granulometry of the handled materials and by the meteorological conditions.

Keywords - Air Particulate Matter, Air Quality, Fugitive Emissions, Loading/ Unloading, Harbour

1 INTRODUCTION

Epidemiological studies have demonstrated that the harmful effects of atmospheric particles in harbours may be originated by the handling of huge amounts of pulverulent raw material (including hazardous chemicals) that are managed in harbour areas in a diversity of loading, transport and storage operations [1-3].

Depending on the material, operation conditions and meteorology, important dust plumes of Air Particulate Matter (APM) can be generated and can have a significant impact on human health at nearby urban areas [4]. In the 80s, the unloading of bulk soybean in the Barcelona harbour caused large increases in the number of asthma patients treated in emergency departments [5]. Similar associations were obtained by Ballester et al. [6] in Valencia and Coruna, Spain. In 2006, in Sines harbour, health authorities stopped an operation of clinker unloading due to the high quantities of emitted dust [7]. Maritime employees may also be exposed to a variety of products that are handled producing occupational asthma [8].

Despite the unquestionable impacts, these emissions are poorly characterized due to the fact that a port has some unique features like (a) many types of non point source activities, (b) large number of handled materials and (c) unique meteorological condition due to the land and sea breeze effects.

These fugitive emissions pose problems both for general air quality management as well as for the operational management of the facilities. Managing local particles concentrations can be a frustrating affair because the weight of these sources could be very high comparing with the local anthropogenic stationary sources. Therefore, emission inventories are basic requirements in formulating environmental management strategy and policy and developing emission control measures for future development. An inventory provides the baseline to create and implement emission mitigation strategies and track performance over time [9].

This study was carried out within the framework of the project $PM_{fugitive}$: Mitigating the Environmental and Health Impacts of Particles from Fugitive Emissions that aims at 1) developing sampling strategies for a proper characterization; 2) performing a chemical, physical and morphological emission characterization; 3) assessing the environmental and health impact of fugitive emissions and 4) suggesting mitigation options.

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The present work, aims at characterizing APM emitted during unloading operations of fertilizer, phosphorite from Syria and phosphorite from Morocco in order to compile an inventory of the main characteristics of $PM_{2.5}$ and $PM_{2.5-10}$. The generated information will be used in a future work to predict the impact of harbour activities in nearby areas by using dispersion models.

2 EXPERIMENTAL

2.1 Harbour operation

Sampling of fugitive emissions was performed in a Portuguese harbour that for confidential reasons can not be identified. The harbour is located in a particularly zone where APM fugitive emissions is a core of environmental concerns. It is an industrial area that coexists with a high density population region and an environmental protected area that belongs to the Natura 2000 Network.

Several experimental campaigns were carried out during fertilizer and phosphorite unloading operations. These operations consisted in a grab that unloaded the material from the ship to a hopper which then introduced the material inside the trucks. Operations started at 8:00 and finished at 24:00 with 2 intervals (12:00-13:00 and 19:00-20:00), except on Sundays.

APM measurements were performed for 6 days, starting on a Sunday (23rd May 2010) which was considered as a reference value because the operations were stopped. Fertilizer (3504 tons) unloading started Monday at 8:00 and finished

Tuesday at 12:00. 4824 tons of phosphorite from Syria started to be handled Tuesday at 13:00 and the operation was completed on Wednesday at 24:00. 7701 tons of phosphorite from Morocco started to be unloaded Thursday at 8:00 and the handling finished Friday at 24:00. On average 230 ton of material were unloaded per hour of operation (Table 1).

2.2 Sampling methodology

The assessment of fugitive emissions is a difficult task because they are highly dependent on the wind direction which can be very variable during one day of operation. In order to overcome this difficulty, two sampling stations were used in parallel in order 1) to minimize the influence of the wind direction in the quantification and characterization of these emissions and 2) to allow the comparison between the emissions provided from the handling of different materials. Sampling points were located 47 meters from the operation area according to Fig. 1. This distance enabled us to preferentially collect the suspended fraction of the handled materials with minor or negligible interferences from particles emitted by other anthropogenic sources.

In addition, one meteorological station measured the parameters wind direction, wind velocity, temperature and precipitation.

The wind rose (red in Fig. 1) shows that during the sampling week the wind direction was predominantly from South West and North West. Therefore, the sampling stations alternated between a facing the wind position and a wind shielded position.

Table 1: Sampling campaign chronology. Type of handled material, operation conditions, $PM_{2.5}$ and $PM_{2.5-10}$ sampling duration and associated average wind direction.

|			Type of material	Operation conditions		Sampling duration (min)	Wind direction (°)
				Unloading (ton)	Operation time (h)		
23 May 10	8:00	12:00	Without				
Sunday	13:00	19:00	handling	-	-	1440	248
	20:00	24:00					
24 May 10	8:00	12:00				234	195
Monday	13:00	19:00	Fertilizer	3504	17	284	184
	20:00	24:00					
25 May 10	8:00	12:00				99	208
Tuesday	13:00	19:00				116	222
	20:00	24:00	Phosphorite				
26 May 10	8:00	12:00	Siria	4824	20	124	196
Wednesday	13:00	19:00				154	248
	20:00	24:00					
27 May 10	8:00	12:00				189	220
Thursday	13:00	19:00				151	299
	20:00	24:00	Phosphorite	7701	30		
28 May 10	8:00	12:00	Morocco			196	324
Friday	13:00	19:00					
	20:00	24:00					
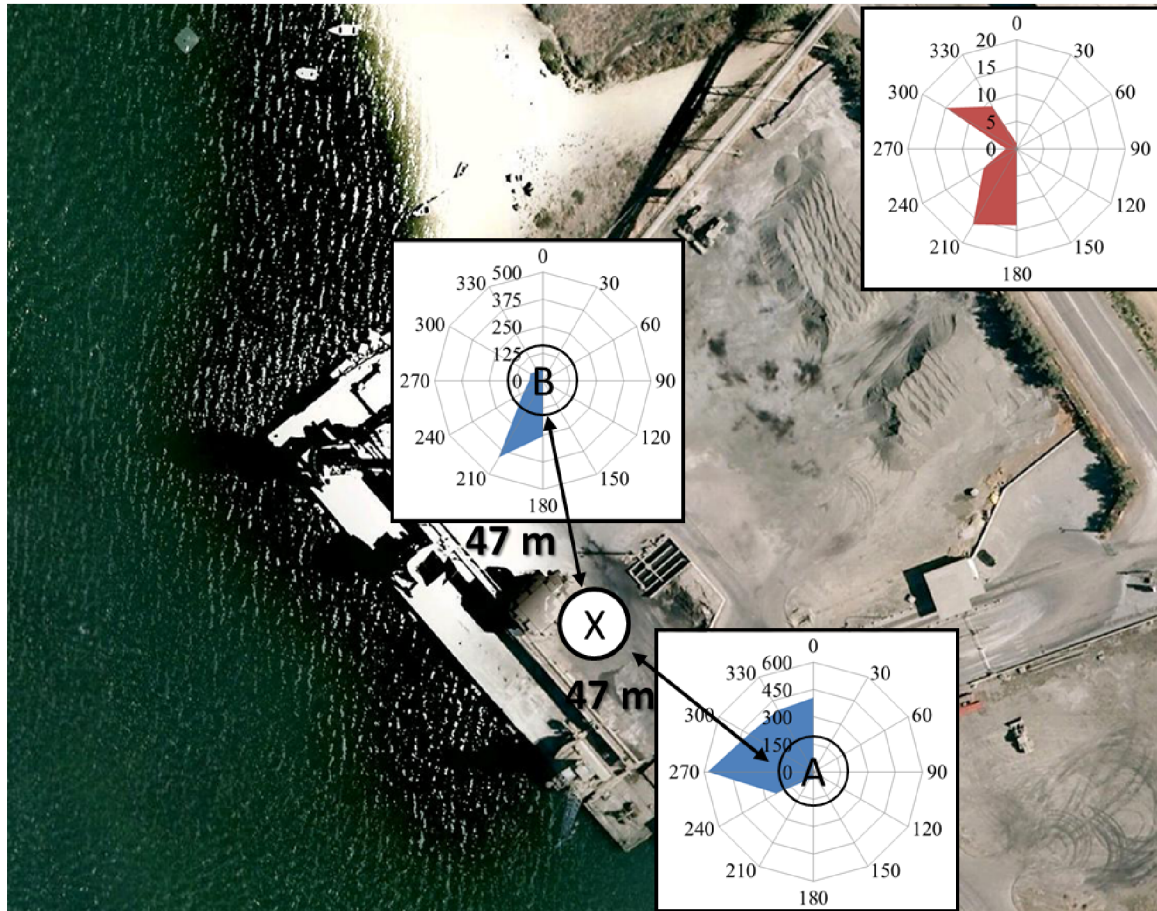
Fig. 1 – Localization of the sampling equipment (A and B) and unloading activities (X). PM_{10} concentrations ($\mu g.m^{-3}$) measured in A and B discriminated by wind direction. Wind rose (red) shows the wind direction during the sampling week.

In order to assess the impact of handling operations two types of equipments were used in each sampling station: Beta Gauge particle monitoring instruments and Gent samplers. Beta Gauge instruments were used in order to monitor continuously (with integration period of 1 hour) the PM_{10} concentration throughout the sampling campaign. These measurements allowed establishing associations between PM_{10} concentrations and the type of operations and meteorological conditions.

Gent samplers were used to perform a chemical characterization of $PM_{2.5}$ and $PM_{2.5-10}$.

Gent samplers were equipped with a PM_{10} pre-impactor stage and with a Stacked Filter Unit (SFU). The SFU carried, in two different stages, two 47 mm Nuclepore polycarbonate filters. Air was sampled at a flux of 15-16 $l.min^{-1}$, which allowed the collection of particles with aerodynamic diameter (AD) between 2.5 and 10μm in the first stage and particles with DA<2.5μm in the second stage [10].

For each handled material 3 sampling periods were performed in 2 parallel measurements (Point A and B) resulting in 12 filters (6 for $PM_{2.5}$ and 6 for $PM_{2.5-10}$).

2.3 Chemical analysis

The filter loads were measured by gravimetry in a controlled clean room (class 10 000). Nuclepore filters were weighted on a semi-micro balance. Filter mass before and after sampling was obtained as the average of three measurements, when observed variations were less than 5%.

Chemical analyses were carried out by Particle Induced X-Ray Emission (PIXE) and k_0-standardized Instrumental Neutron Activation Analysis (k_0-INAA). In ITN, both techniques have already demonstrated to be suitable for non-destructive multi-elemental analysis of APM sampled in the outdoor [11], indoor [12] and industrial environments [13].

Each sampled filter was divided in four parts. For chemical identification one quarter was analyzed by PIXE [14] - to measure the elements Al, Br, Ca, Cl, Cr, Cu, Fe, K, Mn, Ni, P, Pb, S, Si, Ti, V and Zn - and another quarter by k_0-INAA [15,16] - to determine As, Ce, Co, La, Na, Sb, Sc, Sm and U.

PIXE analysis was carried out at a Van de Graaff accelerator, in vacuum and two X-ray spectra were taken for each of the samples; one with a 1.2MeV

proton beam and no absorber in front of the Si (Li) detector for low energy X-ray elements and another with a 2.4MeV proton beam and a 250 μm Mylar® filter to detect elements with atomic number higher than 20. The beam area at the target was 20 mm^2.

For k_0-INAA, the filter quarter was rolled up and put into a clean thin foil of aluminium and irradiated for 5-h at a thermal neutron flux of 1.03×10^{13} cm^{-2}.s^{-1} (f=103.4±1.3; α=-0.035±0.0001; Tn=330°K) in the Portuguese Research Reactor.

After irradiation, the sample was removed from the aluminium foil and transferred to a polyethylene container. For each irradiated sample, two gamma spectra were measured with a hyperpure germanium detector: one spectrum 2-3 days after the irradiation and the other one after 4 weeks. Tests of reproducibility within the filters and between filters were taken, using parallel sampling with two similar sampling units and measuring the particle species by INAA. Results were reproducible to within 5–15%, providing strong support for the validity of the analytical techniques [17, 18]. The accuracy of analytical methods was evaluated with NIST filter standards, revealing results with an agreement of ±10% [19].

Blank Nuclepore filters were treated the same way as regular samples. All measured species were very homogeneously distributed; therefore concentrations were corrected by subtracting the filter blank contents.

2.4 Chemical analysis of bulk material

Three types of bulk materials were handled in the harbour during this work: fertilizer, phosphorite from Syria and phosphorite from Morocco. Pellets of these materials were made and the techniques PIXE and k_0-INAA were used to perform the chemical characterization. The granulometry was assessed by separating the materials in different fractions, sieving them using sequential nylon nets, and by measuring gravimetrically the different size classes obtained.

3 RESULTS

3.1 PM$_{2.5}$, PM$_{2.5-10}$ and PM$_{10}$ levels

Figure 2 shows the PM$_{10}$ concentrations measured by the Beta Gauge instruments placed in Point A and B, from 23 May (00:00) until 28 May (14:00).

As expected, Sunday presented the lowest concentrations because all operations were suspended, including those of maintenance and unloading. Hence, the levels obtained for this day were considered as references values.

The operation of fertilizer discharge started Monday at 8:00. During the handling of this material, the wind direction was predominantly from South West. Consequently, the equipment placed in Point B

registered significantly higher concentrations than equipment B reaching a maximum of 991 μg.m^{-3}. At the end of the day, PM$_{10}$ concentrations decreased due to rainfall (0.77mm between 21:00 and 24:00), the rest of the week was dry. Concentrations measured during fertilizer handling were higher on Monday than on Tuesday. This fact can be explained by the higher average wind velocity measured Monday (2.6 m.s^{-1}) comparing with Tuesday (1.5 m.s^{-1}).

The unloading of Phosphorite from Syria started Tuesday afternoon. The wind that predominantly blew from South West until Tuesday at 21:00, changed the direction to North West. This was the reason for the shift of higher concentrations from point B to point A. The highest PM$_{10}$ concentrations measured during the week were registered for this material (1131 μg.m^{-3} measured in point B).

Wednesday night, during a period without handling operations, very high concentrations were registered. This was due to the resuspension of dust that had been deposited on the ground of the harbour during the unloading operations of phosphorite. Besides the lower wind velocity, this phenomenon was more intense in this particular night. In fact, in the previous day (Tuesday), high quantities of phosphorite were deposited on the ground that was not appropriately cleaned.

The handling of phosphorite from Morocco started Thursday at 8:00. Except on Thursday morning, the winds predominantly blew from North West. Consequently, the highest concentrations were registered in Point A. The maximum concentration measured for this material was 867 μg.m^{-3}.

Gent samplers were used to study the main characteristics of the suspended particles (concentrations, granulometry and element contents) associated with each handled material. In order to minimize the effect of the wind direction, the average of the 6 concentrations (2 samplers × 3 trials per material) obtained for each granulometric fraction was calculated.

Results presented in Figure 3 showed that concentrations varied depending on the discharged material. The highest average concentrations were registered for phosphorite provided from Syria ([PM$_{2.5}$] = 60 μg.m^{-3} and [PM$_{2.5-10}$] = 270 μg.m^{-3}) followed by phosphorite provided from Morocco ([PM$_{2.5}$] = 43 μg.m^{-3} and [PM$_{2.5-10}$] = 100 μg.m^{-3}). The lowest concentrations were registered during the handling of fertilizer ([PM$_{2.5}$] = 19 μg.m^{-3} and [PM$_{2.5-10}$] = 78 μg.m^{-3}).

These operations contributed mostly for the increase of the coarse fraction of PM$_{10}$.
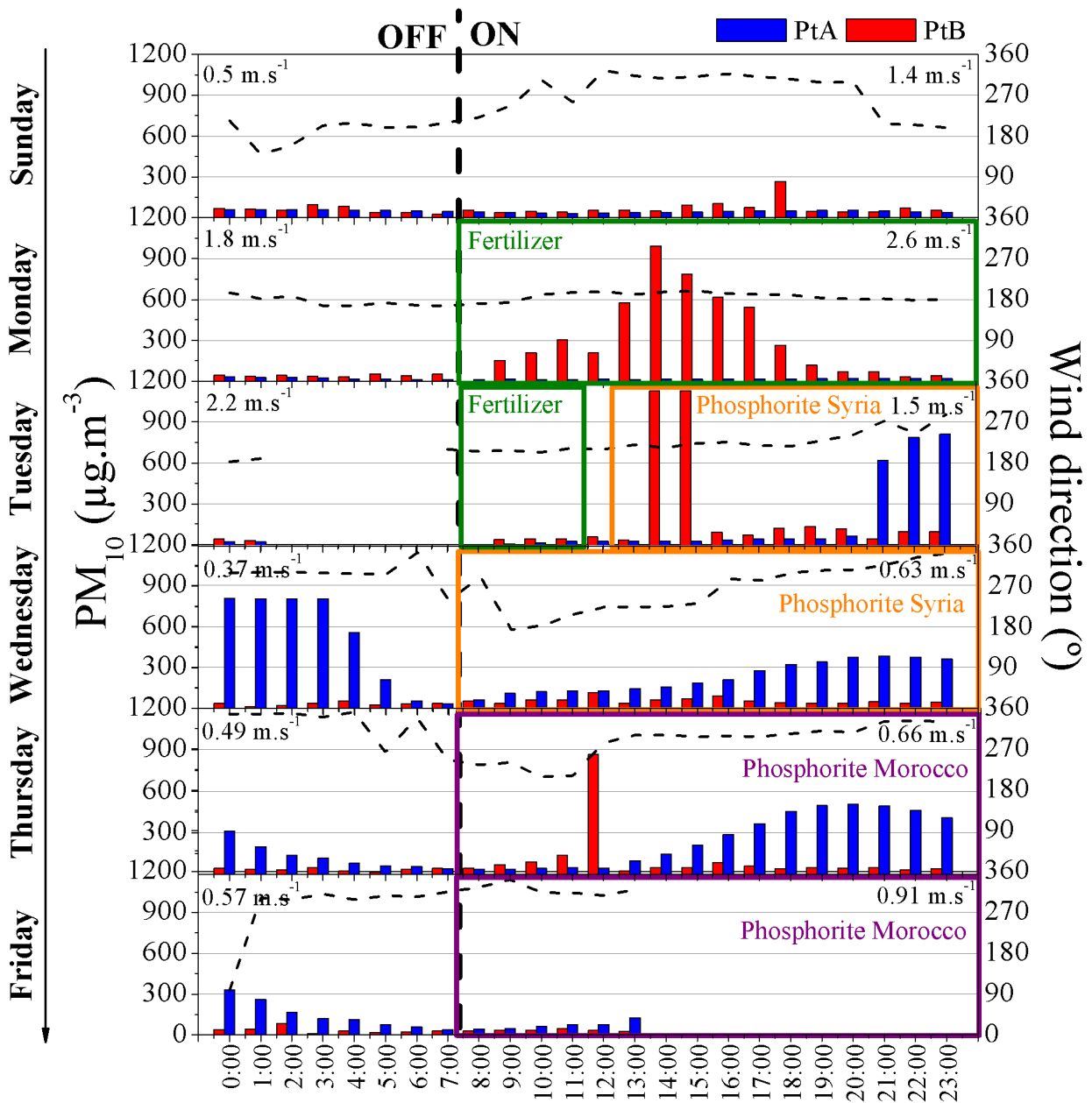
Fig. 2. PM_{10} concentrations measured in harbour in Points A and B ($\mu g.m^{-3}$). ---Wind direction, (°) and average wind velocity for the periods off (0:00-8:00) and on (8:00-24:00) ($m.s^{-1}$).

In order to investigate the impact of these fugitive emissions on the nearby inhabited area, $PM_{2.5}$ and $PM_{2.5-10}$ concentrations for the closest air quality sampling station (8 km) were analyzed for the same sampling period. Results presented in Fig. 3 showed that the concentrations in this sampling station were significantly lower than the ones measured in the port during the handling of material. Moreover, in this urban air quality sampling station, concentrations were higher when the harbour activities were suspended. These results indicated that, besides the high levels of particles measured in the port, apparently this sub-urban area was not influenced. This suggests that large particles are deposited in in the vicinity of the harbour before reaching this sub-urban area.
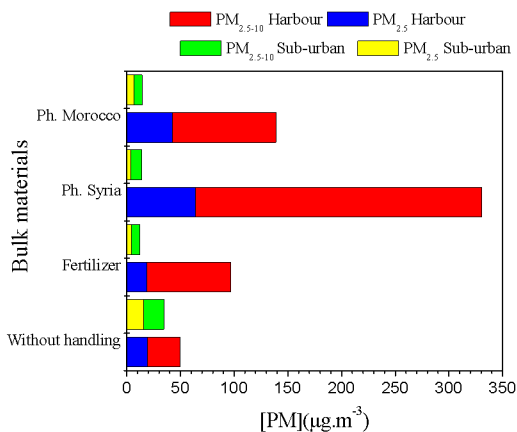
Fig. 3. PM average concentrations measured in the harbour and in a sub-urban background site during the bulk materials handling (values in µg.m^{-3}).

3.2 Chemical Characterization of PM levels

Bulk handled material and suspended particles (PM$_{2.5}$ and PM$_{2.5-10}$) were characterized by INAA and PIXE. A comparative description of the chemical composition of the bulk material and aerosol collected during this campaign is shown in Table 2.

The major constituents measured in fertilizer were Ca (5.3%), Fe (4.2%), K (1.6%) and Na (0.7%). Phosphorite was mainly composed by Ca (30%) and P (9.8%) with a smaller ammount of Si (2.5% or 2.0% depending on the origin). Several works have shown that these elements are important constituents of fertilizers and phosphorites [20,21]. Besides these major elements, Table 2 shows the presence of some toxic heavy metals (As, Cr, Ni, Pb and V) and radioactive elements (like U) in the materials. Some

radioactive elements (like U) in the materials. Some investigators have already demonstrated concern not only about the presence of these compounds in phosphorite, which is used to produce phosphate fertilizers [20-24], but also about the implications they could have for the contamination of the air, soil, water and food chain [22].

As expected, suspended particles measured during the operations reflected the composition of the handled bulk material. In PM$_{10}$ the highest elemental concentration (>10%) was Ca for all associated materials and Cl, K and Na for fertilizer. Concentrations higher than 1% were measured for P, S and Si for all associated materials, Cl and Na for phosphorite, Fe for fertilizer and phosphorite from Morocco, K for phosphorite from Morocco.

A significant increase of some element concentrations was observed while the harbour was operacional (ON) compared to when it was shut-down (OFF).

For phosphorite handling, ratios ON/OFF higher than 10 were registered for the elements Ca, Cr, Br, Ni, P, Pb, Si, V and Zn. Ratios higher than 100 were determined for the elementes Ca (measured in PM$_{2.5}$ sampled during handling of Syria phosphorite) and P (measured in PM$_{2.5}$ sampled during unloading of both types of phosphorite and in PM$_{2.5-10}$ collected when Marocco phosphorite was operated). Ratios higher than 50 were obtained for Cr in all samples collected during the harbour operation. During fertilizer handling higher ratios (ON/OFF>60) were registered for the elements Ca, P, K followed by Cr, Br and Zn with ON/OFF ratios higher than 20. Cu and U, in both fractions, and Ce, Co, Sb, Sc and Sm, in coarse fraction, were only measured during the handling operations [25].

Table 2: Concentrations of major and trace components of bulk handled material and aerosol. Values in mg.kg^{-1}.

| | Bulk Material (mg.kg^{-1}) | | | Aerosol (mg.kg^{-1}) | | | | | | | | |
| | | | | PM$_{2.5}$ | | | PM$_{2.5-10}$ | | | PM$_{10}$ | | |
Element	Fertilizer	Ph. Syria	Ph. Morocco	Fertilizer	Ph. Syria	Ph. Morocco	Fertilizer	Ph. Syria	Ph. Morocco	Fertilizer	Ph. Syria	Ph. Morocco
Al	350	1100	4000	6700	6300	6600	3100	2200	3700	8200	7400	10000
As	14	1.9	18	14	13	15	7.8	2.8	7.6	10	7.3	13
Br	41	2.1	2.1	1900	280	680	430	240	310	2300	470	650
Ca	53000	300000	300000	530000	120000	81000	140000	120000	94000	420000	230000	170000
Ce	90	30	66	35	43	61	19	19	10	15	10	25
Cl	32	910	350	17000	2100	2300	170000	18000	23000	180000	20000	25000
Co	6.4	0.6	0.2	12	22	8.8	10	4.4	4.4	13	13	8.0
Cr	1.7	170	450	1100	250	360	19	220	180	940	390	480
Cu	100		30	860	870	970	250	100	530	700	340	1000
Fe	42000	1200	1800	47000	5500	18000	13000	2700	6400	59000	7300	24000
K	16000	220	600	170000	4800	9700	39000	1100	5100	210000	3700	11000
Mn	16	6.9	17	930	31	600	90	45	140	510	40	390
Na	7700	3600	5500	47000	17000	38000	83000	18000	19000	120000	29000	44000
Ni	4.5	46	95	470	18	400	120	19	85	360	19	390
P	89	98000	98000	16000	42000	21000	24000	32000	26000	20000	75000	47000
Pb	8.9	23	53	1100	250	1800	580	120	280	1300	250	1400
S	300	4000	4900	19000	21000	31000	22000	3600	6400	41000	25000	37000
Sb	500	0.45	2.3	8.5	12	53	5.2	1.5	31	6.5	12	30
Sc	4.3	2.6	10	2.7	2.5	0.77	1.7	4.3	4.9	1.8	2.2	3.4
Si	830	25000	20000	13000	47000	23000	15000	27000	20000	23000	74000	44000
Sm	5.0	3.4	17	2.3	1.7	1.1	60	1.5	3.7	21	1.4	2.0
Ti	13	80	270	2500	90	220	85	55	140	850	49	81
U	40	62	130	25	26	5.0	27	34	55	13	24	37
V		140	380	890	250	130		120	210	300	210	140
Zn	12	330	360	5900	620	2900	1300	420	650	7000	840	3500

3.3 Enrichment factors

The enrichment factor method has been used as an attempt to evaluate the contribution of the bulk handled material for the elements measured in PM_{10}. This methodology - using Crustal Enrichment Factors - is commonly used to calculate the strength of the crustal and non-crustal origin of the elements [26-27]. In the present study, Enrichment Factors were calculated using 1) Uranium (U) as a reference element (EF_U), 2) the bulk material composition present in Table 2 and 3) Eq. (1) (Fig. 4):

$$EF_U = \frac{\left(\frac{[X]}{[U]}\right)_{PM}}{\left(\frac{[X]}{[U]}\right)_{bulk}} \qquad (1)$$

U was used as a reference element because previous studies have already demonstrated that phosphorite and fertilizer are enriched with this element [20-21]. Moreover, U was not detected in filters sampled when the harbour was stopped, whereas average concentrations of 0.73, 6.8 and 6.2 $ng.m^{-3}$ were registered in PM_{10} during the handling of all materials. This shows that local sources other than harbour operations had a negligible contribution for this element in the atmosphere. $EF_U > 10$ suggests that a significant fraction of the element did not stems from the handling of bulk material.

EF_U indicated that during phosphorite handling, the elements As, Ca, Ce, Cr, P, Sc, Si, Sm, Ti, U and V, in PM_{10}, originated mostly from harbour operations. In fertilizer unloading, EF_U were lower than 10 for As, Ce, Co, Fe, Sb, Sc and U, showing that these elements originated mostly from material handling. Besides Ca, K and Na being major elements in the composition of fertilizer, other sources contributed for the presence of these elements in PM_{10}. Ca has a crustal origin and is generated by from cement production [28], coarse K is associated with sea and soil whereas fine K stems from combustions [29] and Na is found in sea-spray [26]. All these sources are present in this industrial area [30-31].

4 DISCUSSION

Several factors contributed to the environmental impact of the emissions originated from the handling of bulk materials in the port. These main factors included: meteorological conditions (wind direction, wind speed and precipitation), characteristics of the handled material and maintenance of the port cleanness.

Results presented in Figure 1, for PM_{10} concentrations discriminated by wind direction,
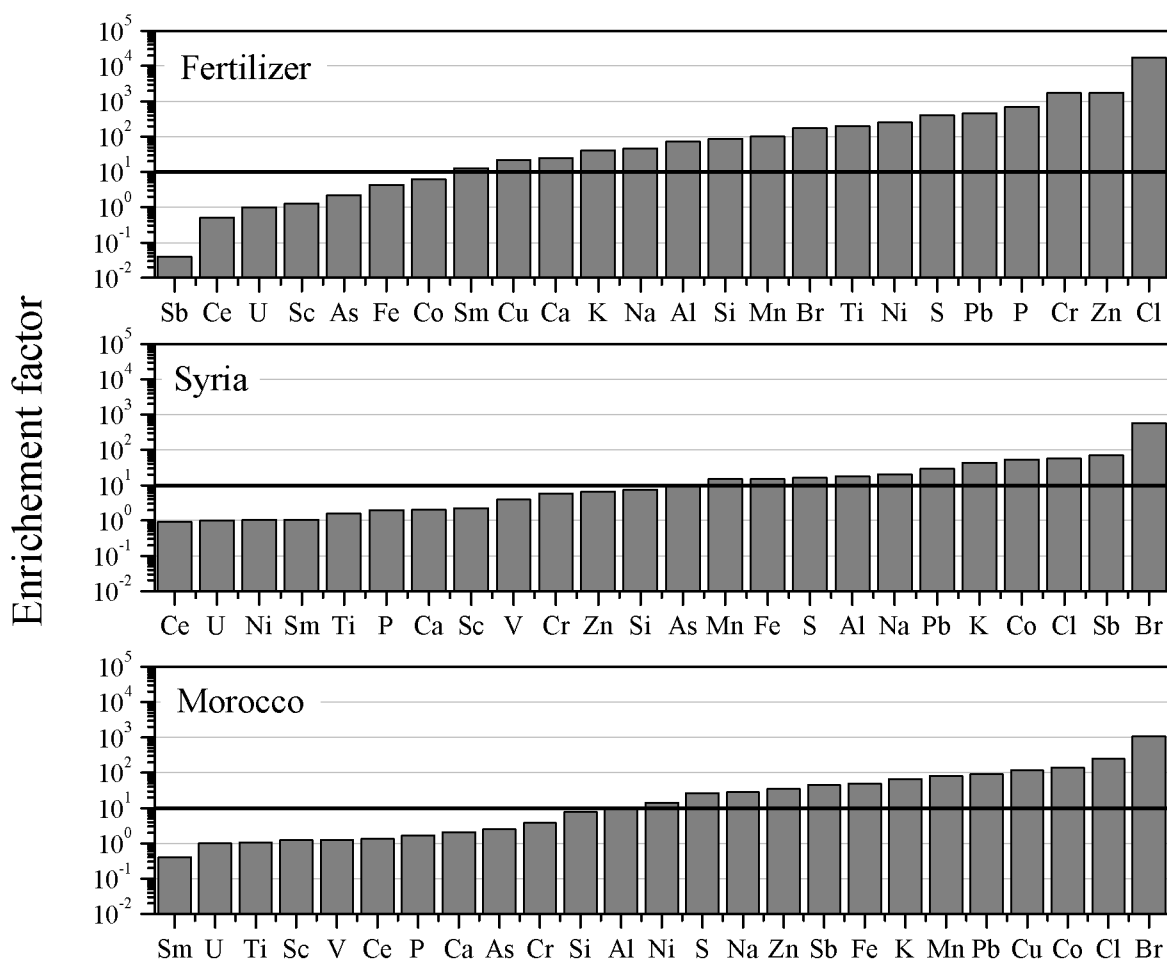

Fig. 4. Enrichment factors using U as a reference element and handled material composition.

corroborate the idea that the location of the sampling stations relative to the wind direction is essential to evaluate the impact of fugitive emissions. In point A, PM_{10} concentrations were significantly higher when wind blew from the North West, whereas in point B the highest levels were registered for South West winds. This fact stresses the importance of performing parallel measurements, using several samplers around the emission source, in the assessment and characterization of fugitive emissions.

Wind speed had also a significant impact on the suspended particles concentrations. This was demonstrated by the variations of PM_{10} concentrations measured during fertilizer handling under different wind velocities (Monday versus Tuesday).

Results showed that emissions produced by unloading operations depend on the characteristics of the discharged material. Significant differences were detected between the phosphorite origin (from Syria and from Morocco) and fertilizer. These significant differences can be explained by the granulometric distributions of the different materials. 70% of the mass of the fertilizer has a diameter between 3.2 mm and 4.2 mm, whereas 80% of the phosphorite mass has a diameter < 1 mm [25]. Results showed a clear relationship between PM and the bulk material composition. The analysed bulk presented relatively high concentrations of known toxic elements, such as As, Cr, Ni, Pb, V and U. Therefore, the high levels of PM_{10} measured during the handling operations may result in very high concentrations of these potential toxic elements.

5 CONCLUSIONS

This study assessed the impact of harbour operations on APM by 1) measuring continuously PM_{10} concentrations, meteorological variables and operation conditions and 2) characterizing the bulk handled materials and suspended particles ($PM_{2.5}$ and $PM_{2.5-10}$) by INAA and PIXE. The main conclusions extracted from this work may be summarized as follows:

- A proper characterization of fugitive emissions should include the use of 1) several sampling points around the operation area and 2) complementary equipments. Parallel sampling measurements will minimize the influence of the wind direction. Complementary equipments will allow the assessment of the influence of meteorological and operational variables on the emissions and the collection of particles for chemical characterization.
- Handling operations should be conditioned by the wind speed, because the present results showed that there was an increase of emissions with the wind speed.
- Resuspension of dust is an important source of particles in the harbour. Therefore the maintenance of the ground cleanness is very important.
- The characteristics of the handled material – granulomery and chemical composition highly contribute to the concentration and composition of suspended particles. Lower granulometries were associated to higher concentrations of suspended particles. The chemical analysis of bulk material and suspended particles indicated the presence of known toxic elements, such as As, Cr, Ni, Pb, V and U.
- In this work, apparently the impact of the emissions for neighbouring populations was not significant. The operations contributed mostly for the increase of coarse fraction of PM_{10} and these large particles tend to be deposited near the emission source.

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