December 2009 Volume 8 Issue 4

Trade Science Inc.

Analytical CHEMISTRY

An Indian Journal

Review

ACAIJ, 8(4) 2009 [640-645]

Air pollution in an oil reffenery case: S.A.M.I.R Sidi Kacem Morrocos

A.Haidar[1], O.Kassou[2], A.Chaouch[1], A.Echchelh[3]*

[1]Laboratory of Applied Chemistry and Quality Control, Faculty of Science BP133, Ibn Tofail University Kenitra, (MOROCCO)

[2]Laboratory Quality Control. Oil refinery SAMIR BP 60. Sidi Kacem, (MOROCCO)

[3]Laboratory for Electrical Engineering and Energy System, Faculty of Science BP133, Ibn Tofail University Kenitra, (MOROCCO)

E-mail : echeladil@yahoo.fr

Received: 17th July, 2009 ; Accepted: 27th July, 2009

ABSTRACT

Preliminary results from this study allow the control of air pollution caused by the Oil Refinery SAMIR, Sidi Kacem, Morocco. The air quality in 2007 in the refinery was generally good. However, it should be noted that the olfactory nuisances (odours) are a form of air pollution immediately perceived by the population of the city hosting the refinery in question. Particulate Dust (large and fine particles), sulphur dioxide (SO_2) and oxides and the dioxide nitrogen (NO and NO_2), symbolized by NO_x, reveal pollution caused by emissions from the refinery's chimneys. The concentrations of the major indicators of pollution were generally less than the limits prescribed by the Moroccan guidelines as well as recent European standards. With regard to sulphur dioxide, we recorded low annual average value at the refinery. But in July 2007 we noticed a considerable excess of a daily average value. The limit values stem from current scientific knowledge and take into account the effects on the environment. The results of this study could be used for the prevention and control of ambient air pollution of the refinery. Thus we can conclude that no adverse effect on public health is to be feared.

KEYWORDS

Air pollution;
Oil Refinery;
SO_2;
NO_x;
Suspended particles.

INTRODUCTION

Faced with the social pressures exerted and governmental standards, the polluting odorant has no choice but to have the pollution it generates reduced if it is wanted to be harmless in the environment that surrounds it. Air for humans constitutes a necessary, vital environment. A normal person breathes on average 15 m3 of air per day and exposes him/herself to pollution caused by the impure airways. The atmosphere is a mixture of nitrogen, oxygen and traces of rare gases; moreover, it contains water vapour, carbon dioxide and traces of 40 other gases. Thus, no absolute composition can be determined. The atmosphere is always more or less polluted. Therefore, the standards of air quality can only be relative and therefore define a set of concentrations of pollutants that are acceptable to a given community[1]. The main sources of air pollution in volumes of emissions are industry and means of transport. All major industries use fossil fuels[2]. In an

Oil Refinery, odorous compounds can be organic or inorganic. There are three main families[3]: Sulphur compounds (hydrogen sulphide, mercaptan, and sulphides), nitrogen compounds (ammonia, amines, heterocycles...) and oxygenated compounds (organic acids, aldehydes, ketones, alcohols). The broadcasts (emissions, issues) of SO_2 oil refineries depend mainly on the content in sulphur of raw products and on the debits (flows) of treatment by fluid catalytic cracking. Hydrogen sulphide is one of the malodorous compounds most frequently encountered. In addition to having a very unpleasant smell, its perception threshold is very low (0.00047 ppm[4]. It is also toxic and corrosive, resulting in some facilities, the deterioration or loss of equipment[5]. However many refineries fuelled by heavy crude are also corrosive Hydro-treatment, reducing their sulphur contents, and thus the emission of SO_2. NO_x projections of the refineries come especially from the fuels furnaces and boilers. While the catalytic cracking fluid is the main source of particles suspended in an Oil Refinery, these emissions result from devices of regeneration of the catalyst of the catalytic cracking[6]. However, today there is not a national or international standard setting values that limit CO_2 emissions. In light of current developing technologies, specific emissions less than 100 kg of CO_2 per tonne of crude processed oil are considered as good practice[7]. The intensive processes of petrochemical industries require sophisticated environmental management to protect water, soil and air from pollution. Odours, and more particularly bad smells, as the dust nuisance are certainly the strongest and most immediately felt in terms of quality of the atmosphere[8]. In this perspective, a quality monitoring network of ambient air in the Oil Refinery SAMIR Sidi Kacem has been established. The aim is to determine the degree and real rates of certain indicators of air pollution and monitor its development. The results of these tests help to determine what measures to take.

MATERIAL AND METHODS

The monitoring of air quality in this site is provided by the quality control laboratory of the SAMIR (Moroccan Limited Company of Industries of Refining), Sidi Kacem and the mobile laboratory LPEE (Public Laboratory of Tests and Studies), which measures pollution by stationary sensors. These sensors allow the continuous measurement of pollutants according to which monitoring is regulated: sulphur oxides (SO_2), nitrogen (NOx) and dust suspensions. This monitoring process is ensured at a station within close proximity to the refinery.

Meteorological parameters

The local and regional weather conditions are essential to explain the quality of the air. They are implicated in the transport, distribution and transformation of air pollutants. The city of Sidi Kacem is located in a region formed by a series of low hills with little hills hollow in the centre. According to the regional meteorological centre in Sidi Kacem[9], the annual average rainfall for 2007 is 450 mm (± 75); 90% of the rainfall is concentrated between October and April. The prevailing winter winds from the west are cold and tepid, while those from the east are, in summer, warm and dry, with an annual average temperature of 27°C (± 3.8) and have oscillated between a minimum of 1° C recorded in January 2007 and a maximum of 45°C recorded in August 2007. The periods of sampling and measurements of ambient air quality at the site of the refinery during the months of February, May, July and November of 2007 have coincided with generally moderate weather. Indeed the sky was usually clear in May and it was relatively cool in February. The annual average relative humidity was 66% and the annual average air pressure was 101 KPa (± 15). In addition, this year was characterized by winds blowing in almost all directions with two main components, the first is oriented towards the South West (SW) and the second is oriented towards the North West (NW). These winds blew at very low speeds ranging between 0 and 3.6 m/s and an average speed does not exceed 0.3 m / s (± 0.08).

Sampling and measurements

Sampling and analyses are conducted two days per month. The companion measures focused on a single sample point located within the refinery, whose polar coordinates are (North 34 ° 13'858, 42'826 ° 05 West). During the monitoring of ambient air quality of the refinery, the methodology used to conduct sampling tests and analyses is as follows: The measurements are continuously made during the day from 8:30 to 17:30;

the concentrations of gaseous pollutants (SO_2, NO., NO_2, NO_x) are given in semi hourly averages (30 minutes) and concentrations of suspended particulate matter (MPs) are quite given in daily averages.

Methods and measuring equipment

The mobile lab is equipped with all facilities required to characterize the quality of ambient air (weather station, sampling device, automatic analyzer of gaseous pollutants, station acquisition and data processing). Nitrogen oxides (NO_x) are measured by an automatic analyzer using the principle of chemiluminescence and according to NFX 43-018 Standard.

In fact:

Measurement of NO (nitric oxide): A sample is placed in the presence of ozone to oxidize NO to NO_2 (nitrogen dioxide) to the excited state (denoted * NO_2). NO_2 * This NO_2* is going to emit an infrared radiation through returning to the fundamental state. The analyzer measures this radiation with regard to the quantity of NO present in the sample.

Measurement of NO_x (nitrogen oxides) and NO_2: Before performing the previous measure, NO_2 is reduced to NO in a molybdenum furnace. This gives us the measurement of NO_x (NO + NO_2).

The measurement of NO_2 is calculated by the difference between the concentrations of NO_x and NO.

Sulphur dioxide (SO_2) is measured by an automatic analyzer using the principle of the ultraviolet fluorescence, according to NFX43-019 Standard: The air sample is illuminated by an ultraviolet lamp. Sulphur dioxide passes to the excited state (* SO_2) by absorbing a part of radiation and by returning to the ground state, emitting a fluorescent radiation of a different wavelength. The analyzer measures the quantity of radiation of fluorescence, which is proportional to the SO_2 concentration.

Regarding diffused dust, measurements are carried out according to NFX43-023 standard, with high volume samplers. Each sampler consists of a suction pump, a flow-meter, a port filter and a filter of glass fibers. The measurement of the concentration of suspended particulate matter in the ambient air is done by gravimetric method, which consists of a weighing of dust on a microbalance. Knowing the volume of air sampled, the difference in weight corresponds to the particles in the air.

RESULTS

Regulatory aspect

TABLE 1 shows a summary of the Moroccan legislation on the quality of ambient air. These are the values of the parameters measured as part of this companion. They are fixed by the decree implementing the Law No. 13-03 on the fight against air pollution.

TABLE 1 : Summary of Moroccan legislation: Law No. 13-03.

parameters	Unit	Annual limit value [(1)]	Limit value semi schedule [(2)]	Imperative limit value [(3)]
Nitrogen dioxide (NO_2)	(µg/Nm^3)	100	200	400
Sulphur dioxide (SO_2)	(µg/Nm^3)	100	200	400
Diffuse dusts (MPs) (4)	(µg/Nm^3)	200	300	400

(1) Arithmetic average of the values semi schedule measured during one year.
(2) 95 % of the semi schedule averages of one year must be lower than this value.
(3) Absolute limit value for health protection, semi Schedule to not exceed.
(4) Values based on averages of 24 hours.

The annual average measurement results, composed of the accompanying elements of quality control of the ambient air of this refinery, carried out during May, February, July and November 2007, are presented in TABLES N°2, N°3, and N°4, respectively relative to the parameters NO_x, SO_2 and MPs.

TABLE 2 : Monthly average measurement results of NO_x

Period	NO_x (µg/Nm^3)			
	Maximum	Minimum	Average	Standard-deviation
February	138	0	35	14,6
May	47,8	0	5,7	3,5
July	49,7	4,1	18,3	2,6
November	48,6	0,7	20,3	1,5
Moroccan Standard		200		****

TABLE 3 : Monthly averages measurement results of SO_2.

Period	SO_2 (µg/Nm^3)			
	Maximum	Minimum	Average	Standard-deviation
February	66,1	0	9	2,5
May	38,2	0,4	7,8	5,4
July	214	1,4	48	26,2
November	98	1,9	24,3	11,4
Moroccan Standard		200		***

TABLE 4 : Monthly averages measurement results of Dust Stream MPs.

Period	Diffuse Dust MPs (µg/Nm^3)			
	Maximum	Minimum	Average	Standard-deviation
February	147	52	100	21
May	160	73	117	54
July	101	91	96	14
November	73	58	66	9
Moroccan Standard		300		***

The results of air quality monitoring for the period from February to November 2007 are presented above for the main pollutants emitted by the refinery, including sulphur oxides, nitrogen oxides and particulate matter.

Sulphur dioxide (SO_2)

Sulphur dioxide is an acid gas soluble in water. It turns little by little to sulphuric acid; it is a powerful, little volatile liquid, and it can persist within the materials practically indefinite[10]. The maximum annual concentration average of (SO_2) measured is 24 (± 17.8) µg/Nm3, much lower than the value limits to be respected (200 µg/Nm^3) (TABLE 5). But daily value, that exceeded this limit were observed, including the highest concentrations that was recorded during the summer period. Indeed, (Figure 1) and (TABLE 3) show significant peak concentrations of SO_2 in July 2007. These peaks indicate pollution by sulphur dioxide emissions generated by air from the chimney of the refinery. A "peak" of SO_2 has been demonstrated up to 214 µg/Nm^3. These levels vary significantly depending on the origin of crude oil. More it is rich in sulphides, and sulphur removal from refinery works well, more smoked refinery emit SO_2. Moreover these values vary remarkably depending on weather conditions prevailing in the station. In summer the accumulation of pollutants due to poor atmospheric dispersion: high concentrations can be accumulated when the plume is trapped in a mixed layer developed in a stable layer («smoking")[11]. Theoretically, the air temperature decreases with altitude. However, when a cold layer of air is below a layer of warm air, there is a thermal inversion. These delays the air mixtures, thus leaving the pollutants accumulate near the surface. Indeed when the wind passing over the hills surrounding the town of Sidi Kacem, with warmer air aloft by the morning sun and cool night air in bottom of valley sheltering the refinery, the air containing fumes cannot mount, so that air pollution is concentrated at the bottom. Eventually, clear skies with a light wind and strong sunshine promote the accumulation of pollutants.

TABLE 5 : Monthly averages of variations of the reviewed parameters; SO_2, NO_x and MPs during the period of the study: year 2007.

Period	NO_x	SO_2	MPs
February	35	9	100
May	5,7	7,8	117
July	18,3	48	96
November	20,3	24,3	66
Minimum	5,7	7,8	66
maximum	35	48	117
Average	20	24,15	93,7
Standard-deviation	12	17,8	21,21

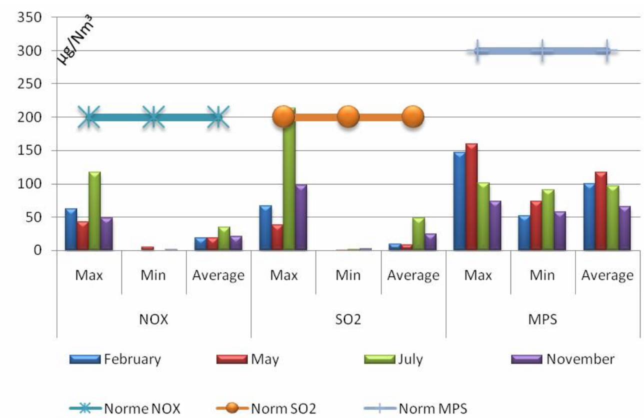

Figure 1 : Monitoring the quality of ambient air from the refinery in 2007.

Oxides of nitrogen

TABLE 2 presents the monthly average concentrations of nitrogen dioxide (NOx). The maximum concentration of NO_2 measured in February 2007 is represented by a peak of up to 138 g / Nm^3; it remains remarkable even if it is less than the maximum daily average fixed by the Moroccan standard (200µg/ Nm^3). However, in the same month, the monthly average value of NO_2 has not exceeded 35 (± 14.6) g / Nm^3. In fact, the oxides of nitrogen are gases that form when the air is raised to high temperatures. NO_2 (+ IV) dioxide or (peroxide) nitrogen gas can be found in the liquid state at temperatures below 21.4 ° C at atmospheric pressure, while the NO (+ II) nitric oxide or nitric oxide was perceived in the gaseous state.

Nitrates also emit such gases. They are soluble in water and form nitric acid (HNO_3) and nitrous acid (HNO_2). Sunshine triggers chemical reactions between various pollutants, through the ultraviolet rays. As indicated by TABLE 5 above, the average value of four companies of the climate control of the refinery, NOx is 20 (±12) g/Nm^3. Beyond the month of February 2007, with its highest monthly average (35 (± 14.6) g /Nm^3), this seasonal phenomenon disappears, oxides of nitrogen are trained at altitude and therefore reduce their concentration in water . The decrease of observed concentrations (Figure 2) is linked to weather conditions. During winter, the vertical circulation of air is greatly reduced by the layer of temperature inversion[12]. Pollutants emitted at low altitude are "prisoners" of the plain. The colder air which is nearer to the ground than the altitude can be maintained several days and blocked between the boundary layer and the free atmosphere. This phenomenon can play the role of a lid. This probably explains the winter maximum daily value in ambient air compared to the rest of the year.

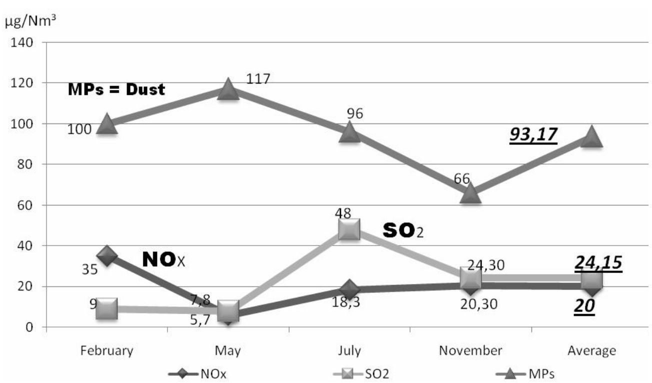

Figure 2 : Spatiotemporal Evolution of the measurements of the monthly averages of parameters: SO_2, NOX and MPs of the Ambient Air of the refinery in 2007

Dust suspended in the air

TABLE 4 gives the summary results of the monthly mean measurements obtained for suspended dust for periods of sampling of four accompanying measuring tests in the year 2007. The daily maximum peak was 160 µg/Nm^3 registered in May 2007. In that same month, we noted a maximum monthly average on the four control campaigns at the level of 117 (±54) µg/Nm^3. This is illustrated in Figure 3) which is below the limit value of 300 µg/Nm^3. Suspended particles are an air pollutant consisting of a complex mixture of organic and inorganic substances suspended in the air in solid and/or liquid form[13]. The fog makes the pollutants in solution in water droplets and keeps them suspended in the air. By contrast, the rain washes the air by precipitating the pollutants on the ground. A slight pollution is mainly due to the activity of the refinery and particularly the catalytic cracking process. Particle size also determines the time of suspension in the atmosphere. In fact, these suspended particles eventually disappear from the air within a few hours after their issuance under the influence of sedimentation and precipitation, as they can remain in the air for days; therefore, these particles can travel long distances. Dry weather in the city of Sidi Kacem encourages flying dust, and the wind transports and disperses it. This explains the meagre changes in concentrations of fine dust in the air. Finally, we must not ignore the pollution caused by motor traffic on the road Sidi Kacem / Tangier in vicinity to the refinery.

CONCLUSION

It is certain that the improvement of the quality of the air of an industrial unit, in particular in urban environment, beyond respecting the guiding values, would allow an important environmental/ healthy gain taking into account the population exposed to such an environmental danger. In the light of the results obtained, the measured average concentrations thus do not have anything exceptional on this industrial refinery that treats approximately 1, 5 million tons of crude oil per year. Even if the average values are reassuring.

REFERENCES

[1] A.Ouédraogo, A.G.Sodré; Afrique Sciences, **3(1)**, 23 **(2007)**.

[2] P.M.Lemieux, C.C.Lutes, D.A.Santoianni; Progress in Energy and Combustion Science, **30(1)**, 1-32 **(2004)**.

[3] Marie-Claude Michel; Traitement de l'Hydrogène Sulfuré par bio- lavage. Mémoire Faculté des études supérieures de l'université Laval pour l'obtention du grade de maître ès sciences (M.Sc.) 95 **(1997)**.

[4] P.Le Cloirec, J.L.Fado, J.R.Degorce-Dumas; Odeurs et désodorisation industrielles. Innovation 128, Paris, 250 **(1991)**.

[5] J.G.Henry, R.Gehr; J.Wat.Pollut.Control Fed., **52**, 2523-2537 **(1980)**.
[6] Environnement Canada: Etude Comparative de la Performance des Raffineries en matière d'Emissions, (conseil canadien des ministres de l'environnement), juillet, **(2003)**.
[7] Coface; Anonyme, lignes directrices environnementales, Extraction, transport, transformation et stockage des hydrocarbures – Raffineries de pétrole. 10, juillet **(2003)**.
[8] R.Bouscaren; Tech.Sci.Meth., **6(3)**, 13-320 **(1984)**.
[9] A.Anonyme; Rapport sur l'état environnementale, Centre régional de météorologie, Souk Lahad, Sidi Kacem, Maroc., 14 **(2007)**.
[10] M.W.Pascoe; La pollution de L'environnement et ses effets sur les documents d'archives PGI-88/ WS/18 PARIS, septembre 1988 Original anglais, 46 **(1988)**.
[11] B.Anonyme; Rapport sur la situation environnementale de, Raffinerie Tamoil. SA de Collombey. Décembre 2005, Département des transports, de l'équipement et de l'environnement Service de la protection de l'environnement., 29 **(2005)**.
[12] C.Anonyme; Tableau de bord santé- environnement, Région Rhône-Alpes, France, L'air, Observatoire régional de la santé Rhône-Alpes, 24 **(2007)**.
[13] OMS; Aide-mémoire Euro/04/05, Centre européen de l'environnement et de la santé de l'OMS, Berlin, Copenhague, Rome, 4, 14 avril **(2005)**.
[14] A.Haidar, A.Echchelh, O.Kassou, A.Chaouch; Etude de traitement des eaux résiduaires de la raffinerie de pétrole SAMIR, accepted and to be printed in PCN at September **(2009)**.