



Study of the impact of heavy metals and physico-chemical parameters on the quality of the wells and waters of the Holcim area (Oriental region of Morocco)

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Abstract

To analyze the impact of heavy metals on well and soil water quality from the Holcime Plant Region, we studied the physicochemical parameters (pH, electrical conductivity, Organic matter, chlorides, sodium, potassium, nitrates, ammonium, sulphates) as well as the evaluation of the degree of metal contamination (iron, zinc, chromium, copper and lead) present in the samples. The analyses carried out revealed low levels of organic matter (MO: max = 1.4 mg / l and mineral matter (conductivity: max = 770 ms / cm.) Analysis of waters of wells and soil showed that grades In NO³⁻ present an average concentration of less than 40 mg / l with temporal variations of remarkable amplitude (in accordance with the standards suggested by the World Health Organization and the Moroccan standards). The average chloride contents do not exceed 783 mg / l (suggested by Moroccan standard). As for nitrous nitrogen, the recorded values showed very low contents and were found lower than the Moroccan standards (0.1 mg.l). Concerning the heavy metals, the examined results showed a significant increase in the concentration of lead in the seven wells, in particular well No. 1 (9.95 µg / l), and an elevation in iron and zinc concentration in the seven wells. The copper and chromium contents were relatively low. In general, the concentrations of these metals at the level of the different samples were found lower than the Moroccan standards (NM 03.7.001, March 2006). In the case of soil analyses, the results showed a high concentration of iron in the seven soil locations, the contents of zinc, chromium and copper remained low, though the lead contents were considerably low.

1. Introduction

Heavy metals are the elements with a density greater than 5 g / cm³. They can be found in air, water and soil. These metals often interfere with the normal course of metabolic processes even in trace amounts [1], causing several diseases and act by accumulation effects [2], with an exception of low tolerable doses. Such metals often have a toxic effect, so their presence in the aquatic ecosystem poses risks to human health and causes harmful effects to living organisms [1]. Besides, industry development has resulted in a significant increase of residues in natural waters and soils, especially those containing heavy metals. Therefore, the determination of the contents of metallic trace elements in water and soil is essential. In addition, legislation on environmental protection is becoming more and more stringent and encourages manufacturers to reduce the concentration of certain metal ions released into effluents [3]. In this context, this paper deals with the impact of metals on the quality of well water and soil of the Holcime factory region, which represent a source of production of these metals during various cement manufacturing processes.

2. Materials and methods

2.1. Description of the study area

2.1.1. Geographic location

The study area is located on the Taourirt-Oujda corridor. The latter is stretched over more than 100 km between Taourirt and Oujda, is generally WSW-ENE-oriented, and limited to the north by the Beni-Bouyahi and Beni-snassen massifs and south by the mountains of Ayat, Zekkara and Touissit-Boubkeur (border of Highlands). The Algerian-Moroccan border artificially defines the eastern limit of the corridor. The corridor offers a relief fragmented by the presence of hills that hamper its topographic regularity [5]. The Holcime factory is located 45 km west of Oujda near the main road Oujda -Casa and 15 km from the town of El Aïoun. This site was chosen mainly for the abundance of raw materials (clay and limestone deposit) and to meet the requirements of the Moroccan oriental market. The main raw materials used in cement manufacture, in particular for the Holcime-Oujda, are limestone (the limestone quarry is 200 meters from the factory) which is extracted by explosive slaughter and clay (which is in 7 km from the plant). Additives are mainly gypsum whose deposit is located 60 km from the plant, while tufa and pozzolan are extracted from several deposits in the region of Nador [4].

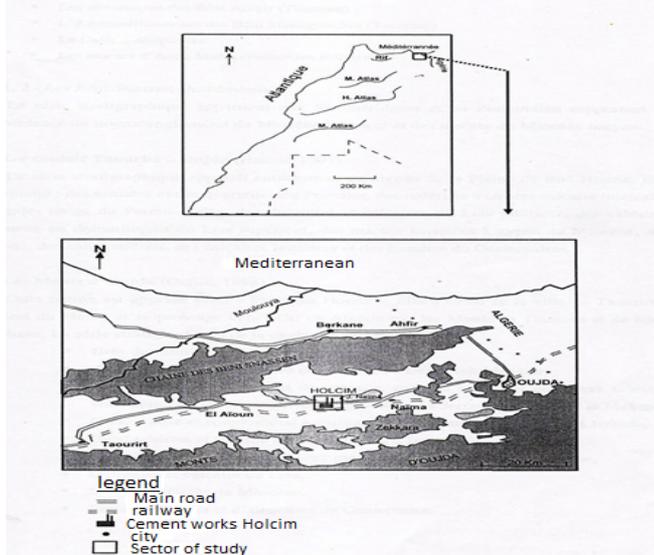


Figure 1 : Sector of study in Eastern Morocco

2.1.2. Geological setting

The study area occupies a very fascinating place in eastern Morocco. It is situated between two parallel mountain ranges dominated by limestone (Fig. 2): The Beni Snassen chain and the Oujda Mountains. Along the Taourirt-Oujda corridor, the stratigraphic series appears entirely at the level of Bou-Houria plain. It includes: primary schist and quartzite, limestone cement dolerites interspersed with Permo-Trias red clay, dolomites and limestone of the lower Lias, marly or dolomitic limestone of the upper Lias, gypsum Miocene, silts, conglomerates, lake limestone and Quaternary basalts [6].

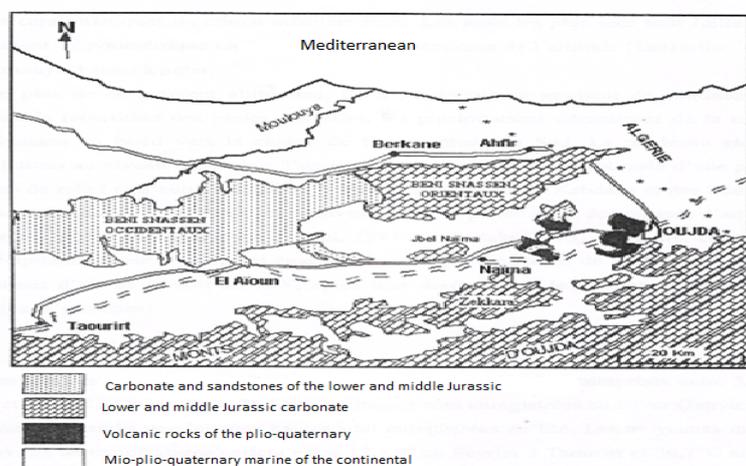


Figure 2 : Synthetic geological map of the study area

2.1.3. Climate framework

The climate of North-eastern Morocco is a Mediterranean climate which is strongly influenced by the Sahara. They go up to less than fifty kilometres from the sea-bed, through the tabular region of Highlands. It is on the other hand a region in a sheltered position compared to the Atlantic influences. The chains of Kabdana, Beni Snassen and Jerada finally play the roles of successive barriers facing the penetration of Mediterranean influence. This is why the climate of the region is defined as being of a continental type. In spite of the proximity of the sea, it demonstrates significant variations due to a succession of contradictory influences over time and rather dry because of the position of a Shelter, behind mountain ranges [5].

2.2. Choice and preparation of samples

To estimate the degree of metallic contamination of waters of wells and ground which surround the Holcime factory, 7 wells and 7 locations from various ground soil locations near each well were exploited.

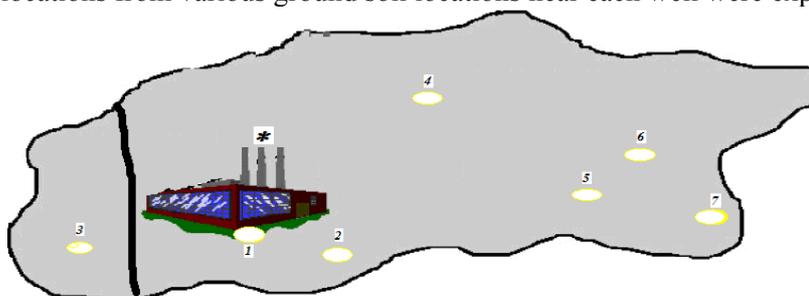


Figure 3 : Location of sampling points of Holcim : **—** : Main road (Casa-Oujda) and *****: Cement Factory (Holcime)

Table 1: Location of sampling points from the factory

Wells	Position by supplying the plant	Distance
1	Factory	-
2	South West	150 m
3	South East	300 m
4	North West	1500 m
5	West	3000 m
6	West	3500 m
7	West	4000 m

All wells have a lid and are on farms except well No. 1 which is located within the plant. For physicochemical analyses: water samples are taken from plastic bottles, well rinsed with distilled water and with the water to be analyzed, at the time of collection. For heavy metal analyses: water samples are taken from 50 ml polyethylene conical tubes; the samples are acidified with 2% nitric acid (HNO₃). Soils were removed from the surface (5 cm thick) using a non-metallic tool and stored in clean plastic bags and kept at low temperature. The soils were dried at 105 °C. In the oven for 24 hours, then ground and homogenized. The samples are stored in special plastic bags to avoid any risk of contamination. Labelling is rigorous to avoid any confusion about the identity of the samples.

2.3. Analytical methods

2.3.1. Principle and procedure of physicochemical parameters

The analyses of the various physical-chemical parameters were carried out according to the method described by Jean Rodier (2011) [7]. Temperature, hydrogen potential (pH) and electrical conductivity were measured at the time of sample collection. PH was measured with the Portable pH-meter field, the type (WTW pH 330i / SET), and conductivity with conductivity meter, type (WTW cond 330i / SET). The temperature was measured by an integrated thermometer in the measurement of conductivity and pH-meter. Nitrate (NO³⁻), Nitrite (NO²⁻), Ammonia nitrogen (NH⁴⁺) and sulphate (SO₄²⁻) are determined by a colorimetric method using a UV / visible spectrophotometer Type of spectrophotometer (JASCO V-530) Calcium (Ca²⁺) and magnesium (Mg²⁺) were determined by the volumetric method with EDTA (ethylenediamine acid), the oxidizability (organic matter: MO) was determined by high oxidation Temperature in acid medium, Total alkalinity (AT) and bicarbonate (HCO₃⁻) are

analyzed by volumetric determination with 0.1N HCl. Sodium (Na⁺) and potassium (K⁺) are determined by exciting atoms by flame type photometer (AFP-100)

2.3.2. Principle and procedure of metallic traces in Waters and soil

The analysis of metals in water and soil is carried out by atomic absorption spectrophotometer. Metal contents such as Pb, Cu and Cr are determined directly by Atomic Absorption Spectrophotometer with graphite furnace (AAS-GF) type Varian 240, Zeeman. Iron and zinc were measured by the AAS flame, the Varian Spectrophotometer type with atomic absorption four (SAAF) type Varian, 240 Sequential fast. The determination of total metal trace elements in the soil samples is carried out by mineralization in closed Teflon "bombs" using a combination of hydrofluoric acid (HF) and regal water (HNO₃: HCl, 1: 3 V / V) to decompose the sample (IAEA method).

3. Results and Discussions

3.1. Analyses of physicochemical parameters

Table 2: summarizes all the results of the physical-chemical parameters found.

	pH	Conductivity (μ s/cm)	MO (mg/l)	AA (mg/l)	AN (mg/l)	TA (F ^o)	TAC (F ^o)	TH (F ^o)	Ca ⁺⁺ (mg/l)	Mg ⁺⁺ (mg/l)	Na ⁺ (mg/l)	K ⁺ (mg/l)	HCO ₃ ⁻ (mg/l)	Cl ⁻ (mg/l)	NO ₃ ⁻ (mg/l)	SO ₄ ²⁻ (mg/l)
Well 1	7.825	770	1.4	0	0.007	0	30.5	25.6	20.04	50.1	87.85	2	378.2	46.15	33.98	36.14
Well 2	7.61	750	0.77	0	0.001	0	27.5	35.2	22.44	71.98	33.33	1	341.6	74.55	32.52	32.89
Well 3	7.784	674	0.77	0	0.001	0	30	35.8	16.83	76.85	21.48	1	420.1	46.15	35.82	27.96
Well 4	7.35	768	0.51	0	0.001	0	29	37.2	41.68	65.17	20.74	1	359.9	53.25	41.34	38.66
Well 5	7.584	710	0.51	0	0.003	0	29	33.8	15.23	72.96	22.96	1	359.9	49.7	36.05	29.62
Well 6	7.444	722	0.58	0	0.001	0	28.5	33.6	28.05	64.69	25.18	1	353.8	49.7	29.99	39.49
Well 7	7.524	702	0.49	0	0.002	0	29	34	32.86	62.74	25.18	1	359.9	53.25	26.14	34.55

3.1.1 Hydrogen potential

The pH of the water measures the concentration of the H⁺ protons contained in the water. It summarizes the stability of the balance between the different forms carbonic acid and is linked to the buffer system developed by carbonates and bicarbonates [8]. The pH values of the water samples vary between 7.35 and 7.82, which qualifies them nearly neutral. Referring to Moroccan standards (NM 03.7.001 March 2006) or the maximum permissible value is between (6.5 < pH < 8.5), 100% of the water analyzed conforms to the quality of the water used for human consumption.

3.1.2 Conductivity

Electrical conductivity refers to the ability of the water to conduct an electrical current. It is determined by the dissolved contents, the ionic charge, the ionization capacity, the mobility and the temperature of the water. Thus, the measurement of the conductivity makes it feasible to appreciate the quantity of the dissolved salts in the water and consequently its mineralization [9]. All the values of the conductivities found (between 674 and 770 μ s / cm) are lower than the maximum permissible value (VMA = 2700 μ s / cm) according to Moroccan standards (NM 03.7.001 March 2006) poorly mineralized.

3.1.3 Organic matter

Organic matter is a parameter that informs the state of water in the well and, on the other hand, promotes the growth of microorganisms that degrade organic matter. In general, low values favour the development of pathogenic germs [10]. For all the samples, the organic matter contents vary from 0.51 to 1.4 mg/l during the study period and the results obtained show that all the recorded values are below the maximum permissible value (AMV=2mg/l) According to Moroccan standards (NM 03.7.001 March 2006).The excess of the organic matter recorded in Well No.1 may be related either to domestic releases or to the industrial activities of the Holcim plant.

3.1.4 Ammonia nitrogen

Ammoniacal nitrogen is one of the links in the complex nitrogen cycle in its primitive state. Ammonia is a water-soluble gas. Ammoniacal nitrogen is therefore a good indicator of pollution of watercourses by organic discharges of agricultural, domestic or industrial origin [11]. In our study area, no trace of this element was reported. Given

that, the maximum permissible value is set to 0.5 mg / l according to Moroccan standards (NM 03.7.001 March 2006).

3.1.5 Nitrous nitrogen

A concentration of nitrous nitrogen greater than 0.10mg / l can lead to the suspicion of a supply of water rich in decomposing organic matter [12]. This content should not be exceeded in the case of water of deep origin. In our study, nitrites were detected in the waters of the 7 wells, have very low levels and are below normal (0.1 mg / l)

3.1.6 Title of Alkalinity (TA) and Title of Complete Alkalinity (TAC)

From the results obtained, we note that the TA = 0 in the seven wells analyzed, that is to say that, TAC = $[\text{HCO}_3^-]$. The results found show that the major alkaline element, which exists, is the bicarbonate HCO_3^- ; it varies from 341.6 to 420.1 mg / l. These results are high because of the calcareous nature that characterizes the soil of the study region.

3.1.7 The total hardness

In most cases the hardness is mainly due to the Ca^{2+} and Mg^{2+} ions, to which Fe^{2+} , Mn^{2+} and Sr^{2+} ions are sometimes added. The variation in total hardness (TH) observed in the waters of the different wells can be related to the nature of the soil in the area. The values recorded in our study exceed the maximum permissible value (AMV = 30 ° F) according to Moroccan standards (NM 03.7.001 March 2006), except Well No. 1. Hence, the nature of groundwater in the region are hard due to the calcareous nature of the parent rock which is rich in Ca^{2+} and Mg^{2+} .

3.1.8 Chloride

Chlorides are widely distributed in nature, usually in the form of salts of sodium (NaCl) and potassium (KCl). They are often used as pollution indicators [13]. In addition, they exist in all waters in variable concentrations. The chloride contents of the analyzed water samples (Table 2) show values ranging from 46.15 mg/l to 74.55 mg/l. The results show that the chloride concentration is less than 750 mg / l VMA according to Moroccan standards Drinking water (NM 03.7.001 March 2006).

3.1.9 Nitrates

Nitrates are important to follow. Indeed, found in excess, they are an incontestable marker of pollution. At the level of the studied waters, the nitrate contents vary between 26.14 and 41.34 mg / l, according to the standards, VMA = 50 mg (NM 03.7.001 March 2006). This alteration of the quality of sinks by nitrates could be attributed to the natural degradation of organic matter or to nitrogenous fertilizers.

3.1.10 Sulphates

Sulphates result from the streaming or infiltration into gypsum grounds. They also result from the activity of some bacteria (chlorothiobacteria, rhodothiobacteria, etc.). This activity can oxidize hydrogen sulphide (H_2S), toxic sulphate [14], etc. According to the results of the samples analyzed (FIG. 6), the values recorded from 27.96 to 39.49 mg / l remain below the maximum permissible value (VMA = 400 mg / l) according to the Moroccan standard relating to the quality of water intended for Production of drinking water.

3.2 Analysis of metallic contamination of water and soil by heavy metals

The results obtained by the analysis of the total zinc, iron, chromium, copper and lead levels in the water and soil samples are shown in Tables 3 and 4.

Table 3: Change in heavy metals in water

Nature Of sample	N ° of well	Metal (µg/l)				
		Zinc	Iron	Chrome	Copper	Lead
Water	1	275	9	2,74	24,84	9,95
	2	586,7	37	2,5	3,34	7,48
	3	61,2	14	3,07	21,3	8,73
	4	17,1	29	3,02	0,9	7,16
	5	16,2	154	2,96	0,32	5,15
	6	22,9	63	2,73	1,58	6,69
	7	32,8	57	2,43	1,42	6,74

Table 4: Change in heavy metals in soils

Nature Of sample	N ° of well	Metal ($\mu\text{g/g}$)				
		Zinc	Iron	Chrome	Copper	Lead
Soil	1	57,667	22091	80,404	48,33	2,730
	2	57,294	10883,15	68,076	46,511	0,572
	3	46,06	12323,4	38,496	38,5	0,563
	4	72,8	14424	29,767	36,67	5,412
	5	46,832	10703,62	9,955	29,412	0,701
	6	51,201	11463,52	35,365	35,587	0,601
	7	64,614	23209,1	25,454	68,181	1,264

The results of the analyses of trace metallic elements in the examined water samples show an important increase in the concentration of lead in the seven wells, in particular well No. 1 ($9.95 \mu\text{g/l}$), and a rise in concentration of iron and zinc in the seven wells, while the copper and chromium contents are relatively low. Generally, concentrations of these metals in the various samples are below the Moroccan standards (NM 03.7.001 March 2006). In the case of soil analyses, the results show a high concentration of iron in the seven soil locations, the contents of zinc, chromium and copper remain low, but the contents of lead are considerably low.

3.2.1 Total zinc levels in the analyzed waters

The obtained results show that the total zinc contents in the analyzed waters are high, varying between $17.10 \mu\text{g/l}$ and $586.7 \mu\text{g/l}$, the values recorded in the different wells are lower than the maximum admissible value (AMV = 3 mg/l) according to Moroccan standards (NM 03.7.001 March 2006). It is also worth noticing that the highest contents are in the surroundings of the factory, which could be explained on one hand by the dust and the waste emitted by the factory (zinc stemming from the incineration of tires) and, on the other hand, by the geologic nature of the ground and the existence of the main road (Casa Oujda) next to the study site.

3.2.2 Total zinc contents in the analyzed soils

The results obtained show that the total zinc contents in the analyzed soils are high, ranging from $46.06 \mu\text{g/g}$ to $72.8 \mu\text{g/g}$. The high soil levels analyzed could be explained by dust, waste and the sprays emitted by the factory, transported by the wind and the washing of the road which brings quantities of this metal stemming from tires of vehicles.

3.2.3 Total iron contents in the analyzed waters

The obtained results show that the total iron contents in the analyzed waters is variable, varying between 9 and $154 \mu\text{g/l}$. The values recorded in the different wells are lower than the maximum admissible value (AMV = 0.3 mg/L) according to Moroccan standards (NM 03.7.001 March 2006). The variation of the iron contents at the wells analyzed could be explained by piezometry and the mineralogical characteristics of rocks.

3.2.4 Total iron contents in the analyzed grounds

The results obtained show that the total iron content in the soils analyzed is very high, especially in samples No. 1 and No. 7, ranging from 10.703 to $23.207 \mu\text{g/g}$. The high soil levels analyzed could be explained by the dust, waste and aerosols emitted by the plant, the mineralogical characteristics of the soil, and the use of organic fertilizers for the enrichment of iron soils. Iron concentrations are higher at points 1 and 7. These results suggest that the physicochemical conditions of the soil (Redox potential, humidity, etc.) and morphological conditions (presence of obstacles, flows, etc.); have been more favourable to the fixation of iron by the different components of the soil.

3.2.5 Total Chromium levels in the analyzed waters

The obtained results show that the total chromium contents in the analyzed waters are low, varying between 2.43 and $3.07 \mu\text{g/l}$, the values recorded in the various wells are below the maximum admissible value (VMA = 50 mg/L) according to Moroccan standards (NM 03.7.001 March 2006). The low contents of the analyzed waters could be explained by the impermeability of the soil layers.

3.2.6 Total chromium contents in the analyzed soils

The results obtained show that the total chromium contents in the analyzed waters are high, ranging from 9.955 to 80.404 $\mu\text{g} / \text{g}$, and concentrations decrease with the increase in distance from the plant. This increase in chromium levels in the soils analyzed could be explained by the dust and aerosols emitted by the plant and transported by the wind that does not manage to throw them further, the mineralogical characteristics of the soil could be an important cause.

3.2.7 Total copper contents in the analyzed waters

The results obtained show that the total copper contents in the analyzed waters are low, varying between 0.32 and 24.84 $\mu\text{g} / \text{l}$, the values recorded in the different wells are lower than the maximum admissible value (VMA = 2mg / L) according to Moroccan standards (NM 03.7.001 March 2006). The contents in well No. 1 and No. 3 are higher relative to other wells. It might be explained by the leaching of the copper-rich soil from the industrial waste from the Holcime plant.

3.2.8 Total copper contents in the analyzed soils

The results obtained show that the total copper contents in the analyzed soils are high, ranging from 29.412 to 68.181 $\mu\text{g}/\text{g}$. This increase in Copper levels in the soils analyzed could be explained by the dust and aerosols emitted by the plant transported by the wind and by the use of organic fertilizers which enrich the soil copper.

3.2.9 Total lead levels in the analyzed waters

The results obtained show that the total levels of lead in the analyzed waters are very high, varying between 5.15 and 9.95 $\mu\text{g}/\text{l}$. The values recorded in the different wells are lower than the maximum acceptable value (VMA=10 $\mu\text{g}/\text{l}$) according to Moroccan standards (NM 03.7.001 March 2006). Such concentration may be due either to the leaching of the lead-rich soil or to industrial discharges from the Holcime plant. Their contents in the well No. 1 are too high and the maximum permissible value (AMV = 10 $\mu\text{g} / \text{l}$) has been reached.

3.2.10 Total lead levels in the analyzed soils

The results obtained show that the total levels of Lead in the analyzed soils are variable, ranging from 0.563 $\mu\text{g} / \text{g}$ to 5.412 $\mu\text{g} / \text{g}$. The levels of lead in the soil analyzed could be explained on the one hand by the dust and aerosols emitted by the plant transported by the wind and on the other hand, by the use of organic fertilizers which enrich the soils, which often contain lead contamination.

Conclusion

Through various kinds of emissions, the cement industry (similar all other industries), contributes to the alteration of air and soil quality, which would have repercussions on the various components of the receiving environment. The soil, which occupies a privileged place through its role as an interface between the atmosphere, the biosphere and the geosphere, is particularly sensitive to this pollution, along with the underground water. In the present work, the obtained results by the evaluation of the quantity of heavy studied metals (iron, zinc, chromium, copper and lead) accumulated in waters and grounds of the region of the factory Holcime, allowed us to discuss the following observations:

An important presence in the soil for all the trace metal elements studied which presents a contamination of this soil that will have an impact on human health through agric-food products.

A variable presence of the trace metallic elements studied in the waters does not exceed the maximum permissible values according to Moroccan standards for the quality of the water for human consumption, but these levels may increase due to the activities of the plant, which have become increasingly important due to the increased demand for cement.

At the end of this work, we propose the following recommendations to limit the pollution generated by the cement industry:

- Repair dust removal systems after each failure.
- Protection of pollution sources (chimneys, careers) by trees in order to reduce the effect of wind on dust.
- Use closed and well-sealed storage for fuel deposits and cement manufacturing materials to curb dust dispersion.
- Installation of new technologies such as electrostatic filter and bag filter on chimneys.

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