

Physicochemical characterization and Analysis of total metal concentration of grease and wastewater samples: Case study for two wastewater treatment plants in the North of Morocco: Tangier and Tetouan

H. Kabbaj¹, H. El Mai², M. D. Galindo-Riãno², M. Stitou¹

¹Laboratory for Water Sciences, Research and Environmental Analysis, Chemistry Department, College of Sciences, University Abdelmalek Essaâdi, B.P. 2121, Mhannech II, 93002 Tetouan, Morocco ² Analytic Chemistry Department, College of Sciences, University of Cádiz, Polí-gono Rí-o San Pedro, 40th Floor P.O. Box 40, 11510, Puerto Real, Spain

Received 26 March 2014; Revised 5 June 2014; Accepted 6 June 2014. **Corresponding author: Email: hindkabbaj@hotmail.fr*; *Tel :(* +212 674 465 517)

Abstract

In this paper, physicochemical characterization and analysis of total metal concentration of greases and wastewater samples from two wastewater treatment plants in the North of Morocco, Tangier and Tetouan, were carried out. The samples were taken in the winter period of the year 2011-2012. For two case studies of wastewater treatment plants in Tangier and Tetouan (WWTP-TG and WWTP-TT), waste solid grease samples were collected from the degreasing tank belonging to the wastewater pre-treatment step. The physico-chemical parameters analyzed for the two stations were selected to determine biodegradable and non-biodegradable organic pollution such as Biochemical oxygen demand BOD_5 (mg O_2/L) chemical oxygen demand (COD g O_2/Kg), and the dosage rate of nitrate $[NO_3^-]$ (mg/L), nitrite $[NO_2^-]$ (mg/L), phosphate $[PO_4^{3-}]$ (mg/L) and organic matter. An analysis of total metal concentrations for Cu, Zn, Cr, Pb, Ni, Tl, Cd, Ba, As, Se, Ag, V, Co, Fe and Mn was performed by inductively coupled plasma mass spectroscopy (ICP-MS) and Inductively coupled plasma atomic emission spectroscopy (ICP-AES). The results indicated the presence of all of the studied heavy metals. In general, the metal pollution obtained in the Tetouan treatment plant (WWTP -TT) is double or higher than that obtained in the Tangier treatment plant (WWTP -TG) with few exceptions. Notably, in both types of samples analyzed for each treatment plant (greases and wastewater), the metal pollution is more concentrated in the solid fraction (grease) than in the liquid fraction (wastewater), with both samples containing a high concentration of similar metals (in mg/kg) Cu, Mn, Zn and Fe for the two wastewater treatment plants (WWTP-TT and WWTP-TG). Grease, a by-product of wastewater treatment, is a hazardous waste, and thus a cause for serious consideration, especially in light of the 28-00 law enforced in Morocco in 2006.

Keywords: Greases, Wastewater, Treatment Plants, Characterization, Heavy Metals,

1. Introduction

This study aims to provide baseline data on the chemical and metal pollution contained in the wastewater and grease samples found at the treatment plant's entry point in order to underline the importance of decontamination and treatment of these pollution sources as well as to alert the appropriate environmental regulatory agencies about the need to formulate an environmental action plan and implement a comprehensive legal framework with the goal of protecting the environment and public health and envisioning a sustainable environment.

Industrial activity is the main source of wealth in developed countries and those in developing countries. However, in most cases, industrial growth is accompanied by problems of pollution and environmental degradation due to the discharge of polluted wastewater. The increase in industries and population growth in the world, as well as the increased use of fertilizers and pesticides in agriculture, have led to a huge growth of contaminating waste, which must be well managed to avoid the transfer of environmental pollution [1].

It should be noted that in Morocco, 80% of domestic and industrial wastewater from urban and rural areas, are released into the environment without any type of treatment [2]. Rivers and streams directly receive 30% of the

total pollution generated by humans [3]. Various studies have shown that some estuaries and rivers are contaminated by heavy metals from waste released by humans [4, 5].

The economic and social development of Morocco will be accompanied by an increase in solid waste (grease). The accumulation of sewage sludge and waste from the sewage system constantly represents an increasing problem because the sludge is stored in an open space and the disposal of residues of bio-waste can cause pollution if they are not treated in an acceptable way [6]. The greases removed from the degreasing tank belong to the sewage sludge. The latter is a heterogeneous mass of liquid in which solids of different sizes are dispersed. Municipal waste sludge contains heavy metals, macronutrients, and micronutrients, traces of elements, organic pollutants, microorganisms and parasitic eggs [7].

There are different types of pollution, in particular chemical, physical, radioactive and biological pollution. This research concentrates mainly on the study of the organic and metallic contaminants in greases and wastewater (collected in the pre-treatment step) from wastewater treatment plants in two Northern Moroccan cities (Tangier and Tétouan). The purpose of this study is to investigate mainly the organic parameters and the total concentrations (mg/kg dry matter) of metals Cu, Zn, Cr, Pb, Ni, Tl, Cd, Ba, As, Se, Ag, V, Co, Fe and Mn to assess and quantify the organic and metallic pollution, and learn about how urban and industrial activities may generate this pollution. Another aim of this paper is to study the transfer of pollution in the solid and liquid phases of the samples collected. Lastly, the study presents a comparative study of the metallic and organic pollution in the two Moroccan cities of Tangier and Tétouan.

2. Materials and Methods

2.1. Areas of study:

2.1.1. WWTP of Tetouan:

The treatment plant in Tetouan is located between the cities of M'diq and Fnideq, with an area of 6 ha. It covers the sanitation needs of a population of about 170,000 inhabitants, with an endowment of 183L/hab/day and a daily flow 31200m³/day. The wastewater in this station is based on the activated sludge process: the wastewater passes through four main steps. The schematics of the wastewater purification process, the line treatment of sludge in the WWTP in Tetouan, is presented in Fig.1. Wastewater arriving in WWTP passes through a coarse grid, a fine grid (step A), aerated sand grid and degreasing tank (step B). After that, the pre-treated wastewater is drained away into the settling tank (step C) where wastewater will receive primary treatment. The water is then treated by an activation sludge (step D) before being treated in the clarification and disinfection tank by chlorine gas (step E).





Figure 1: Schematic of the treatment of the wastewater, grease and sludge at the WWTP Tetouan, Morocco.

2.1.2. WWTP of Tangier:

The water-treatment plant of Tangier was installed on a platform on the sea, little more than a hectare 1ha. It is responsible for the primary treatment of the city's water after filtration. The processing capacity is about 3.8m³/s of water, is 218.000m3/d. First, wastewater is filtered by special railings (step A) before it passes through a purification process to eliminate waste, unrefined sands and oil: grit and grease removal (step B and Step C), which allows for the elimination 80-90% of fats and floating materials. After its passage through pre-treatment step, wastewater is pumped in a marine envoy of 2.3 kilometers and is then rejected into powerful sea currents up to 42 meters deep. These currents create an admixture of effluents and prevent the polluted waters from returning. The schematics of the wastewater purification process in WWTP in Tangier, is presented in Fig.2.

WWTP of Tangier:



Figure 2: Schematics of the treatment of the wastewater and grease at the WWTP Tangier, Morocco.

2.2. Greases sampling:

The same method was used to collect the grease samples in both stations. The greasy waste is collected from the degreasing tank belonging to the first step in the wastewater treatment process (pre-treatment). The collection of greasy waste was taken from the degreasing tank in the pre-treatment stage at the WWTP in Tetouan (position B, Figure 1) and Tangier (position C in figure 2). In the degreasing tank, the greasy and oily material contained in wastewater floats on the surface of the pond and creates a thick layer of fat. The latter is eliminated from the pond by an automatic scraping that works periodically. As a result, the greasy coating is sent to a storage truck, without any conditioning or processing, and transported to a public dump.

When they arrive in the laboratory, the samples are immediately filtered in succession in two Büchner funnels of various diameters (Assistent, 9mm-3mm). The pH and conductivity levels are then noted for every sample, and the filtered samples are conditioned until they reach a pH value of about 2, at which point they are preserved in a freezer at a temperature of approximately 4°C. Before preservation, the grease samples are divided into two parts: the first is reserved for the identification of the physico-chemical properties, and the second, for the determination of heavy metal content and organic matter.

2.3. Physico-chemical characterization:

In order to make a physico-chemical characterization of the studied samples, a solution was prepared with 30g of the greasy sample. The resultant solution is then adjusted to 500 ml using deionising water from a Milli-Q Integral Water Purification System. In each of the samples, the following parameters were determined:

- BOD₅: Biochemical demand oxygen, Standard Instrumental Method [8], using the VELP Scientifica device, BOD Sensor System (S/N: 78531, 2W, 50Hz, 25A).

- DCO: chemical oxygen demand, AFNOR-NF T90-101 [9], and the reading of the measure was taken using the automatic device DCO-71686 (Aqua Lytic, COD Vario).

- NO_3 : nitrate, standard Method [10] and NO_2 : nitrite, standard colorimetric Method [11], PO_4^{3-} : phosphates, Standard colorimetric Method [12], the measures were made with the help of a UV spectroscopy machine (Varian-50 Conc, Visible UV spectrometer).

2.4. Analysis of organic matter:

The chemically modified materials are constituted by organic matter in the sediment, soil or mud called humic substances [13, 14]. These substances have a great influence on the chemical and physical properties of the samples such as water holding capacity, ion exchange capacity, etc. One of the fundamental characteristics of humic substances is their ability to interact with clay, metal ions, oxides and hydroxides to form soluble or insoluble associations, which defines the formation process of metal complexes [15].

The organic matter content is usually determined by the weight loss resulting from the calcination of the sample between 400 and 600°C[16, 17] using a particle size fraction < 2 mm . Thus, for the determination of this parameter, this analysis was quadrupled for each sample (Tetouan, Tangier) using a measure of 0.5g of previously homogenized grease waste to prevent the aggregation and the heterogeneity of the sample. After homogenization, the eight grease samples were placed in tarred porcelain crucibles and pre-calcined in a muffle furnace at 550°C for 30 minutes. The samples were then cooled within a crucible from the desiccator, and upon reaching room temperature, were removed and weighed again in order to repeat the calcination process until the samples reached a constant weight. The organic matter from the collected samples may then be calculated from the difference between the initial weight and the calcined weight.

2.5. Analysis of heavy metals in greases and wastewaters:

The determination of the heavy metal content of the greasy samples is preceded firstly by the pre-treatment of samples. These underwent a vacuum filtration (Fisherbrand, FB-70155), passing through a filter with a membrane of 0.45 μ m, so as to separate the liquid phase (wastewater) from the solid phase (grease). The filtrate was placed in 500 ml sterile Teflon bottles with 600 μ l HNO3 of suprapure for the purpose of preservation, whereas the solid phase was placed onto Petri dishes and oven dried for 24 h. at 60°C [18].

2.6. Samples of wastewaters :

To determine the total content of heavy metals in the wastewater, the standard method EPA-3015 [23], which is based on the microwave digestion of the aqueous samples containing solid materials in suspension, was applied. The measures of concentrations of Pb, Cd, Ni, Co, Cr, Tl, Ag, V and Ba was made by Inductively coupled plasma mass spectrometry (ICP-MS), whereas the analysis of the contents of Zn, Cu, Fe and Mn was made using Inductively coupled plasma atomic emission spectroscopy (ICP-AES, PerkinElmer precisely, AS800 Autosampler).

2.7. Samples of greases :

The heavy metal content was only measured for the samples' lower fraction of 63μ m. In this fraction, almost all of the organic matter and heavy metals are concentrated in accordance with the studies of different authors [19, 20]. The samples were passed through a nylon sieve CISA 63μ m to separate the finer fractions, and to ensure the homogenization of the study material [21, 22].

Metal concentrations of Zn , Pb , Cd , Cu, Fe , Ni, Co , Cr, As, Se , Tl , Ag, V , Mn and Ba were determined using the microwave digestion protocol which is validated by the measurement of concentrations of Zn , Cd , Pb , Cu , Ni and Co in two reference sediment samples: one estuarine sample (SRM-1646a) and one marine sample (GBW-07313). These results are presented in tables 1 and 2 below. An adequate recuperation percentage (estimated at $87\% \pm 10\%$) was measured using a inductively coupled plasma mass spectrometry (ICP- MS, Franklin, Thermo Elemental, 220V- 30Amps -60Hz) and maximum sensitivity instrumental conditions.

Metal	Total Concent	Recuperation $(\%)$	
	certified value	Experimental value	
Со	5	3.76 ± 0.03	75.1
Ni	23	21.66 ± 0.77	94.2
Cu	10.01 ± 0.34	10.64 ± 0.54	106.3
Zn	48.9 ± 1.6	49.90 ± 2.52	102.1
Cd	0.148 ± 0.007	0.12 ± 0.04	82.1
Pb	11.7	11.35 ± 0.25	97.0

Table1. Validation of the analysis of the total content of heavy metals in the reference sample SRM-1646a based on the microwave digestion protocol and measured by ICP-MS

Table 2: Validation of the analysis of the total content of h	eavy metals in the reference sample GBW-07313
based on the microwave digestion protocol and measured b	y ICP-MS.

Metal	Total Concer	Recuperation (%)	
	certified value	experimental value	
Со	$76.7 \pm 1,2$	59.56 ± 1.18	77.7
Ni	150 ± 4	159.71 ± 1.03	106.2
Cu	424 ± 8	400.13 ± 2.77	94.4
Zn	160 ± 3	169.52 ± 1.75	105.9
Pb	29.30 ± 1,1	26.96 ± 0.85	92.0

3. Results and discussion

3.1. Physico-chemical analysis of greases:

The results of the physico-chemical characterization are presented in Table 3. The observed values of pH, conductivity, COD and BOD₅ for the two samples of greases studied are almost equal, which points to a similar composition in biodegradable organic matter and oxidizable matter. However, the concentrations of the elements responsible for eutrophication (total phosphorus and nitrogen), are higher in the grease from the treatment plant in Tetouan compared to that in Tangier.

The concentrations of nitrates obtained: $[NO_3^-]$ (mg/L), $[17.36]_{TT}$ and $[4.78]_{TG}$, may stem from several sources, among them fertilizer runoff, domestic wastewater (detergents) and /or alkaline industrial wastewater [24].

The very high values of the BOD_5 and the DCO obtained in this work imply a strong level of organic pollution most likely due to anthrophic activity upstream from both of the water-treatment plants studied. This high level of pollution is caused by the organic and/or toxic molecules put out by human, industrial, agricultural or domestic activities.

Doromotors	Samples of greases		
Farameters	Tetouan	Tangier	
pH	6.61	6.04	
Conductivité (ms/cm)	35	45.12	
DBO ₅ (mg d'O ₂ /L)	1110	1162.5	
DCO (mg/L)	6224.17	5186.25	
$[NO_3] (mg/L)$	17.36	4.78	
[NO ₂ ⁻] (mg/L)	28.88	7.53	
$[PO_4^{3-}] (mg/L)$	11.44	3.28	

Table 3: Physico-chemical characterization of greases from the pre-treatment of wastewaters from the WWTP-TT and WWTP-TG.

3.2. Analysis of organic matter:

The analysis of the organic matter content is a key parameter to assess, since the metal retention usually occurs during the formation of organic compounds [15].

In the samples collected in the pre- treatment of wastewater (degreasing stage), this parameter showed very high values, with percentages of 73.8 % and 72 % for the grease samples belonging to treatment plants in Tangier and Tetouan, respectively. The high concentration of the organic matter in both stations gave us a preliminary idea about the rate of concentrations of heavy metals contained in the greasy samples of both treatment plants.

3.3. Analysis of heavy metals in greases and wastewaters:

Heavy metals are dangerous for live organisms because of their stability, high toxicity and tendency to accumulate in the ecosystem [25]. Some metals are subject to biochemical transformations, and can create metal organic complexes that are much more toxic than their inorganic forms. Since water is the most endangered part of the ecosystem, it is extremely important to purify wastewaters loaded with heavy metals before the waters are released into natural regions. The toxicity of heavy metals can be listed in order of decreasing toxicity as follows Hg>Cd>Cu>Zn>Pb>Cr>Al>Co - though this is only an approximation as the vulnerability of species to individual metals varies according to the environmental conditions that control the chemical speciation of the metals [26].

The concentration value of each metal presented in this study (derived from wastewater and grease samples) from the two cities was obtained by calculating the average of four measurements (repeated four times for precision) taken with an ICP device.

3.4. Heavy metal content in greases

The analysis of heavy metals conducted on the greasy samples taken from the WWTP-TT and from the WWTP-TG, is presented in the Tableau 4 below. This study reveals the presence of all of the metallic elements studied in this work for both water-treatment plants. The variation of the concentrations of heavy metals, changes from one metal to the other within the same grease sample, though the trend of the variation of the metallic elements is almost the same in both stations. The heavy metal contents of grease from the city of Tetouan, are higher than those from the city of Tangier, save the Cd (mg/kg): ($[0.26]_{TT} < [0.37]_{TG}$) and Se (mg/kg): ($[0.73]_{TT} < [1.20]_{TG}$). This result affirms the results obtained from the DOC (mg d'O₂/l) and MO (mg/l) parameters studied in the previous sections, and shows that the grease samples from the city of Tétouan have a high level of metallic pollution greater than that of Tangier, which may be due to the source of wastewater that eventually finds its way to each station.

The water-treatment plant from the city of Tétouan receives wastewater from nine pumping plants belonging to four tourist zones (Restinga 1 and 2, Puerto Marina and Kabila), four big urban areas (Oued Fnideq, Rifiyin, Somaya and Mellaliyin) and an industrial zone [27]; whereas the water treatment plant from the city of Tangier receives wastewater from urban areas.

Matal	$C(mg/Kg) \pm SD^*$		
Metal	Tetouan	Tangier	
Cd	0.263 ± 0.041	0.375 ± 0.042	
Со	2.022 ± 0.063	1.578 ± 0.032	
Ni	8.463 ± 0.192	5.135 ± 0.305	
Se	$0,730 \pm 0.071$	1.201 ± 0.213	
Tl	0.080 ± 0.003	0.047 ± 0.001	
Ag	1.745 ± 0.097	1.729 ± 0.096	
As	2.960 ± 0.088	1.523 ± 0.087	
Cr	17.556 ± 0.290	15.376 ± 0.107	
Pb	24.041 ± 1.219	18.978 ± 0.399	
Cu	49.593 ± 1.744	38.287 ± 1.216	
V	17.510 ± 0.294	13.264 ± 0.189	
Mn	101.386 ± 1.208	39.628 ± 0.592	
Ba	81.473 ± 1.797	54.767 ± 0.532	
Zn	231.438 ± 3.643	146.662 ± 3.236	
Fe	4689.980 ± 64.570	2071.566 ± 16.265	

Table 4: Total metal content of each of the metals	analyzed in bo	th grease	samples studied.
---	----------------	-----------	------------------

* SD: Standard Deviation

The metallic pollution of both grease samples from the water-treatment plant of the city of Tetouan and Tangier was divided into 3 degrees of concentration (high, moderate and weak). Five heavy metals showed a high concentration pollution: Cu (mg/kg): ([49.59]_{TT} > [38.28]_{TG}), Ba (mg/kg): ([81.47]_{TT} > [54.76]_{TG}), Mn (mg/kg): ([101.38]_{TT} > [39.62]_{TG}), Zn (mg/kg): ([231.43]_{TT} > [146.66]_{TG}), Fe (mg/kg): ([4689.98]_{TT} > [2071.56]_{TG}). The metals exhibiting a moderate pollution concentration are Ni (mg/kg): ([8.46]_{TT} > [5.13]_{TG}), V (mg/kg]): ([17.51]_{TT} > [13.26]_{TG}), Cr (mg/kg): ([17.55]_{TT} > [15.37]_{TG}), Pb (mg/kg): ([24.04]_{TT} > [18.97]_{TG}). Finally, a weak pollution concentration was found in the following metals As(mg/kg): ([2.96]_{TT} [1.52]_{TG}), Co (mg/kg): ([2.02]_{TT} > [1.57]_{TG}), Cd (mg/kg): ([0.26]_{TT} < [0.37]_{TG}), T1 (mg/kg): ([0.08]_{TT} > [0.04]_{TG}), Se (mg/kg): ([0.73]_{TT} < [1.20]_{TG}), Ag (mg/kg): ([1.74]_{TT} > [1.72]_{TG}).

These results are presented in Figure 3, which organizes the polluting metals according to their degree of concentration in both grease samples collected:

WWTP-TT:	Fe > Zn > Mn > Ba > Cu > Pb > Cr > V > N	i >	As > Co > Ag > Se > Cd > Tl
WWTP-TG:	Fe > Zn > Ba > Mn > Cu > Pb > Cr > V > N	>	$Ag > Co > As > Se > Cd > TI_{Degree of}$
			metallic

[Heavy Metals]_{High} [Heavy Metals]_{Medium} [Heavy Metals]_{Low} Pollution **Figure 3:** Metallic pollution concentration of the various heavy metals in the grease samples from the WWTP-TT and the WWTP-TG.

3.5. Heavy metals content in wastewaters :

The analysis of heavy metals in the samples of wastewater taken from the WWTP-TT and the WWTP-TG, is presented in the Figure 5 below. The results obtained in this analysis indicate the presence of all of metallic elements studied for water-treatment plants (Tetouan and Tangier).

Matal	$C (mg/L) \pm SD^*$			
Metal	Tetouan	Tangier		
Cd	0.044 ± 0.001	0.019 ± 0.001		
Со	0.146 ± 0.003	0.097 ± 0.002		
Ni	0.725 ± 0.021	0.364 ± 0.011		
Se	0.037 ± 0.002	0.009 ± 0.000		
Tl	0.003 ± 0.000	0.001 ± 0.000		
Ag	0.0004 ± 0.0000	0.0002 ± 0.0000		
As	0.147 ± 0.011	0.033 ± 0.003		
Cr	0.835 ± 0.015	0.536 ± 0.034		
Pb	0.463 ± 0.010	0.678 ± 0.024		
Cu	11.237 ± 0.208	2.529 ± 0.053		
V	0.586 ± 0.005	0.361 ± 0.011		
Mn	21.379 ± 0.276	10.721 ± 0.225		
Ba	0.077 ± 0.001	0.030 ± 0.003		
Zn	49.406 ± 0.736	10.721 ± 0.225		
Fe	569.054 ± 7.766	240.642 ± 5.815		

Table 5: Total metal content of each of the metals analyzed in the two wastewater samples collected.

* SD: Standard Deviation

The heavy metal contents in the wastewater from the city of Tétouan, are higher than those from the city of Tangier, save the Pb (mg/kg): $([0.46])_{TT} < [0,67]_{TG}$). However, the majority of the metallic elements have weak concentrations. These results are presented in Figure 4, which organizes the polluting metals by degree of concentration in both wastewater samples:

WWTP-TT:	Fe > Zn >	> Mn > Cu >	Cr > Ni > V > Pb > As > Co > Ba > Cd > Se > Ag > TI	
WWTP-TG:	Fe > Zn ≥	> Mn > Cu >	Pb > Cr > Ni > V > Co > As > Ba > Cd > Se > TI > Ag	Degree of
	[HM] _{High}	[HM] _{Medium}	[Hea∨y Metals]⊾₀w	metallic Pollution

Figure 4: Metallic pollution concentration of the various heavy metals in the wastewater samples from the WWTP-TT and the WWTP-TG.

3.6. Discussion about concentrations of heavy metals contents in grease and wastewater

The main sources of heavy metals in wastewaters and sludge are commercial, domestic [28]. Industrial processes of metal finishing and galvanization, mining, chemical agents for plant protection, traffic, municipality waste and

military industry represent the most common sources of pollution with heavy metals [29]. All these sources of pollution are present in the area of the town of Tetuan and of tangier.

The elevated concentration of Zn (5945 mg/kg) was recorded in the both of samples collected (wastewater and grease). Zinc may occur from the process of galvanization, metal treatment, from traffic, from corrosion and leaching of plumbing, water-proofing products, medicines, deodorants and cosmetics, dyes and pigments, printing inks, batteries, plastics and rubber, paper, building materials, etc. [30]. Usually, more than 50% of pollution by Zn occurs from unidentified sources [28]. In this case, airport is suspected as the main source of pollution by Zn.

It has been reported that a contamination by Cu is more associated to domestic sources in comparison with other heavy metals [28]. Sources of Cu are as follows: contamination in the process of galvanization, copper fittings in plumbing, metal processing, fungicides, pigments, wood preservatives, larvicides, brass and other alloys, commercial heating systems and agro-technical use [30]. Possible sources of pollution by Cu in this case were households, (metal processing) and flooring factory.

The Ba, are used as detergents in lubricants. Ba is a typical additive metal in engine and transmission oils, but also a contaminant in drilling applications.

Possible sources of chromium are cleaning products, oils and lubricants, paints and pigments, alloys, pesticides and gardening products [30]. The most chromium contamination arrives from unknown sources [28]. In this case, rain water was considered as a main contributor to pollution by Cr.

The most obvious sources of Pb are lead pipes, which still exist in drainage systems. Other possible sources may include old paint pigments, various varnishes, roofing, cable covering, traffic and even body care products ([30]; [31])

Possible sources of Ni are certain alloys used in sanitary equipment, inappropriate disposal of used Ni–Cd batteries and paints (households, Air Force Mechanics, run-off).

As and Se are potentially dangerous metalloids coming mostly from natural sources. Pollution with As may also arise from old paints and pigments, washing products and from wood preservatives. was always present in eluates. Se may come from food industry and food processing, then from shampoos and other cosmetic products [30].

Possible sources of Cd may be Ni–Cd batteries, paints and photography. The main source of Cd in wastewater are diffuse sources such as processing of food, detergents, body care products and storm waters ([31]), [32], [33]). In this particular case, the most obvious sources of Cd were households and car service stations (run-off).

3.7. Comparison of metal content in grease and wastewater:

During the wastewater treatment in a water-treatment plant, the residual water loses almost all of its metallic pollution before being discharged into the natural environment, in accordance with the section of Moroccan law 28-00 that deals with wastewater treatment. Metallic pollution degrades during the treatment procedure or is transferred and concentrated depending on the specific stage of the treatment of residues (grease and sludge) from the wastewater treatment process. The comparison between the heavy metal contents of wastewater with that contained in the greases for both case studies (WWTP-TT and WWTP-TG), confirms the above and shows that the concentration of metallic levels of pollution are higher in the solid matter (grease), than in the liquid matter (wastewater). Figure 5 (below) exemplifies a comparison between metallic pollution concentration of three metallic elements (Mn, Cu, Zn) in wastewater and grease samples from the water-treatment plants in Tétouan and Tangier.

Conclusion and recommendations

Nowadays, grease is not eliminated properly, but is rather stored and accumulated in landfills temporarily without consideration for its adverse effect to the environment. The physico-chemical characterization and diagnosis of heavy metal content of grease samples from both treatment plants Tetouan and Tangier studied in this work show high levels of metallic and organic pollution in both cities (biodegradable & chemical) with an overload of pollution at the Tetouan station.

The Moroccan law n°28-00 on waste management and disposal requires the treatment or recycling of any waste affecting the environment or the public health and prohibits waste disposal or landfilling into the middle natural areas without treatment. Unfortunately, there is still no legislative text addressing the specific case of greases and indicating acceptable discharge characteristics.

J. Mater. Environ. Sci. 5 (5) (2014) 1622-1632 ISSN: 2028-2508 CODEN: JMESCN

Authorized institutions must make a responsible decision on the greasy waste that is increasing not only in these two treatment plants, but also in other industrial and municipal stations across Morocco.

Urgent and adequate strategies and legal frameworks towards sustainable sludge, bio-wastes, etc. Future efforts should be collaborative and should include all stakeholders in the sector. Furthermore, future research should focus on the development of new alternative treatment methods for both water and greases.



Figure 5: Comparison between the metallic pollution in wastewater and grease samples from both water-treatment plants (Tétouan and Tangier).

References

- 1. Benhamou, Y., Rodríguez-Barroso, M. R., Quiroga, J. M., García-Morales, J. L., El Moumnin, B., *Residuos.* 96 (2007) 62-71.
- 2. Cerezo Monje B., Espino Ramírez R., Silvera Roig C. Informe del agua en Marruecos. Agosto (2011) 113.
- 3. Barakat, A., El Baghdadi, M., Rais, J., Nadem, S., Environ. Earth. Sci., 4 (2012) 797-806.
- 4. Mhamdi, A.A., Choura, M., Maanan, M., Zourarah, B., Robin, M., *Environ. Earth. Sci.*, 61 (2010) 275-286.
- 5. Naoura, J., Benaabidate, L., Black. Sea/ Medit. Environ., 17 (2011) 193-202.
- 6. Wang, M.J., Sci. Total. Environ. 60 (1997) 197:149.
- 7. Alloway, S.J., Jackson, A.P., Sci. Total. Environ. (1991) 100:151-76.
- 8. Rodier, J., Analysis of water, natural water, wastewater and seawater, Dunod, ISBN: 2-04-010045-8, (1978), 559p.
- 9. Standard AFNOR, NF T90-101, determination of the chemical oxygen demand, Dunod, ISBN: 2-04-010045-8, (1988) October.
- 10. Rodier, J., Analysis of water, natural water, wastewater and seawater, Dunod, ISBN: 2-04-010045-8, (1978) 191-193p.
- 11. Rodier, J., Analysis of water, natural water, wastewater and seawater, Dunod, ISBN: 2-04-010045-8, (1978) 160-162p.
- 12. APHA, AWWA, WPCF, Standard Methods for the examination of water and wastewater.17 Edition, (1992) 4-199.
- 13. Förstner, U., Environ. Analy. Chem. 51 (1993) 5-23.
- 14. Grousset, F.E., Jouanneau, J.M., Lavaux, G., Latouche, C., Coast. Shelf. Sci. 48 (1999) 401-414.
- 15. Stevenson, F.J., Wiley. Inter. Sci., (1982).
- 16. Dean, W.E., J. Sediment. Petrol., 14 (1974) 242-248.

- 17. Peiro, L.A., Methodology for the study of heavy metals in sediments. PhD thesis. Chemical Institute of Sarria. Barcelona, (1988) pp280.
- 18. OSPAR JAMP., *Guidelines for Monitoring Contaminants in Sediments* (agreement 2002-2016) (http://www.ospar.org/content/content.asp?menu=00900301400135_000000_000000).
- 19. Förstner, U., Wittmann, G.T.W., Heavy metal pollution in the aquatic environment (2nd Ed). Spring-Verlag. Berlin. Heidelberg New York, (1981) pp 486.
- 20. Sakai, H., Kojima, Y., Saito, K., J. Water. Res., 20 (1986) 559-567.
- 21. Vesk, P.A., Allaway, W.G., Aq. Bot., 59 (1997) 33-44.
- 22. Uriarte, A., Franco, J. Borja, A., Water. Sci. Technol., 37 (1998) 55-61.
- 23. Klitzke, S., Lang, F., Environ. Qual., 36-4 (2007) 1187-1193.
- 24. Billen, G., Garnier, J., Diagnostic biogeochemical functioning of estuary-panache of the Seine. Report Seine-Aval (2005) 17p.
- 25. Krogmann, U., Boyles, L., Bamka, W.J., Chaiprapat, S., Martel, C.J., Water. Environ. Res., 71-5 (1999) 692–715.
- 26. Gray, N.F., Water technology an introduction for environmental scientists and engineers. 2nd ed. Maryland Heights (MO): Elsevier Science & Technology Books, (2005).
- 27. AMENDIS, Veolia Environment, Annual report, Veolia info Retrospective, (2009) 40p.
- 28. ADEME. Metallic micro-pollutants in sewage sludge from urban treatment plants. Technical guide. Angers (France): French Environmental and Energy Management Agency, (1995).
- 29. Bogut, I., Hrvatske. Vode., 5-20 (1997) 223-9.
- 30. Thornton, I., Wilderer, P., Marani, S., Braguglia, D., Palerm, C.J., Pollutants in urban wastewater and sewage sludge (final report), Office for Official Publications of the European Communities. Luxembourg (2001).
- 31. Chauhan, A.S., Bhadauria, R., Singh, A.K., Lodhi, S.S., Chaturvedi, D.K., Tomar, V.S., *Chem. Pharm. Res.* 2-6 (2010) 92–7.
- 32. Veeken, A., Hamelers, B., Sci. Total. Environ. 300 (2002) 87-98.
- 33. Wang, C., Hu, X., Chen, M.L., Wu, Y.H., Hazard. Mater., 9 (2005)119-245.

(2014); http://www.jmaterenvironsci.com