Assessment of the Degree of Contamination by Metal Traces Element (Cd, Zn, Cu, Pb) in the Environment of an Open Landfill of a Large City—Part One : A Human Population

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Abstract: The disposal of urban or hospital waste in open landfills is the easiest way to throw back of them without environmental concerns. MTEs (Metal Trace Elements) are the most toxic mineral elements. This study evaluates the impact of MTE on a neighboring human population or playing near a municipal dump. Two panels were composed of adult men and children (males under sixteen years old). Four trace metal elements were analyzed: copper, lead, cadmium and zinc. The site of the study was the municipal waste dump in Marrakech (Morocco). The results reveal abnormal concentrations of these MTEs in blood and hair of adults and children.

Key words: Humans, metal traces element, contamination, open landfill.

1. Introduction

Contamination of the environment by many potential toxic agents became an obvious evidence. Thus, a growing interest has been shown in recent years to study the potential impact of environmental degradation on human health, and for the development of xenobiotic screening techniques. Two approaches to monitoring can be used to measure and control the exposure of human populations to industrial or environmental contaminants. When it comes to measuring the overall environmental impact in populations exposed to chemical pollution, dander (hair, nails) are excellent indicators of metal exposure, as they present the property to bioconcentrate some metals (eliminating certain toxic is among other dander), and avoid the use of other techniques such as taking blood or urine

analysis. Appendages are easy to use [1]. They retain and can trace the history of the exposure due to continued growth. They have the unique property of being non-stressful markers of repeated or chronic exposure to further establish the long-term consumption profile. The municipal open landfill of Marrakech in Morocco was chosen as the pilot for authors' study.

2. Materials

2.1 The Human Panel

The study focuses on a panel: a target panel, noted panel C, composed of 67 volunteers (all male) who stayed for more than a year in two villages in Harbil¹, the region associated with a witness panel, noted panel W, away from the influences of the discharge of the

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¹ Harbil: a douar 14 km far away from Marrakech on the road to Safi, near the landfill of the city; each family has a member on contact with the discharge.

Table 1 Sampling of the two human panels.

	Hairs	Blood
Panel C	12 children	12 children
	50 adults	28 adults
Panel W	14 children	36 children
	30 adults	55 adults

city of Marrakech (35 km south of the city composed of 91 individuals (all male) for a natural physiological reason, separating people into two classes: adults (over 16 years old) and children (under 16 years old). Two targets were selected for this study: the human blood (internal target) and dander (hair, outdoor target).

Table 1 shows the sampling of two targets in the two panels.

2.2 Geographical Study Sites

A common control area was chosen for the study of human populations. This is the remote area Aitourir from sources of contamination by MTE (Metal Trace Element), located 35 km east of the city of Marrakech on the road to Ouarzazate.

It seemed interesting to compare the results of contamination by MTE from two different sources of pollution from the waste incineration of human activity (artificial contamination) and the operation site Draa Lasfar mine located approximately 10 km to the West of the city of Marrakech (natural contamination) [2]. The two sites are sufficiently far apart to avoid self-contamination.

3. Technics: Samples and Mineralization

3.1 Biological Samples

Samples of blood and hair taken from smokers (tobacco and herbal drugs) and among alcohol drinkers are eliminated since these two factors are involved in the evolution of metal contents in subjects [3, 4]. Indeed, alcohol or tobacco consumption can increase by 2.5 to 4 times the cadmium levels in blood.

3.1.1 Hair Samples

In order to highlight an acute or chronic

intoxication or detect a deficiency of micronutrients (zinc, copper) [5, 6], analysis of the concentrations of minerals in integuments and more particularly in hair is the most common means of assessing the level of impregnation of the body. The hair samples are simpler to implement, more accepted, and their cut, transport and storage are easy to be compared to that of biological fluids. Their mineral levels are generally high, simplifying their dosage and promote quality results [7, 8].

Approximately 10 g of hair of each participant are taken at the neck and immediately packaged in paper envelopes numbered to know the age and place of main activity of each individual. Taking hair samples tests was conducted in a panel near the discharge panel which previously named “panel C” and was compared with the test taken by a panel unrelated discharge panel previously named “panel W”. Panel C consists of sixty-two individuals spread between twelve children under fifteen and fifty adults; the control panel consists of forty-four individuals spread among fourteen children under fifteen and thirty adults.

3.1.2 Blood Samples

The main objective of this part is the determination of the MTE loading in the human panel. The study focused on the C panel consisting of forty individuals, divided between twelve children under fifteen and twenty-eight adults. The results are compared to a male witness panel ninety-one individuals spread between fifty five adults and thirty-six children.

3.2 Mineralization and Dosing

3.2.1. Hair Samples

From washed hair [2, 9] with nitric acid 10% four

times for 10 min then rinsed with acetone three times for 10 min and dried, a test portion of approximately 50 mg is weighed exactly and then introduced into a polystyrene tube and added with 1 mL of nitric acid 8N [3, 10, 11]. The sealed tube is kept at room temperature for 24 hours; during this preliminary phase, the bulk of the sample is dissolved in the acid. The resulting liquid takes a yellow tint more or less dark, in hair coloring [12], and a viscous consistency. To complete the dissolution, clogged tubes are placed for 1 hour in a water bath at 60 °C [10]. The plugs are held in place by pressure (plate and weight). The determination of Cd, Cu, Pb and Zn traces is carried out by atomic absorption spectrometry in flame mode.

3.2.2 Blood Samples

A test sample of approximately 1 mL of whole blood was dried in an oven at 85 °C. Mineralization is then performed by an attack with nitric acid (1 mL) overnight [4, 13, 14]. The digests thus recover are completed to 10 mL with double-distilled water and stored in a refrigerator at 4 °C pending assay AAS (Atomic Absorption Spectroscopy) flame method [4, 13, 15-17].

4. Methods: Statistics and Pollution Index

4.1 Standard Deviation

In the general case of n measurements and a_i

$$PI = \frac{\text{content of a MTE in the studied environment}}{\text{content of this element in the reference environment}} \quad (5)$$

5. Results

5.1 Hair Samples

The results are reported in Table 2.

The average content of Cd 2.66 ± 0.24 ppm for adults in the study area is relatively high compared to that seen in children 1.96 ± 0.10 ppm in the same area. These two values are significantly large relative to average levels noted in the panel control 0.37 ± 0.07 ppm and 0.43 ± 0.04 ppm respectively in children and adults in the same area.

The average values found in the panel studied are

(concentrations) having of equal accuracy ($\forall i, p_i = 1$, [18]), the weighted average value $\hat{y}$, in a distribution, is given with its standard deviation experimental m that captures the quality of the distribution. The weighted average value $\hat{y}$ is the likely average value of measured values:

$$\hat{y} = \frac{\sum_{i=1}^n a_i}{n} \quad (1)$$

This standard deviation is statistically calculated with the relationship:

$$m = \left[\frac{1}{n-1} \sum_{i=1}^n (a_i - \hat{y})^2 \right]^{1/2} \quad (2)$$

The average error of the estimate can be given by Eq. (3):

$$m_{\hat{y}} = \frac{m}{\sqrt{n}} \quad (3)$$

The approximate value is the value to be measured can be given as:

$$y = \hat{y} \pm m_{\hat{y}} \quad (4)$$

4.2 Pollution Index

The pollution index, noted PI, is used to quantify the pollution. This PI is calculated by the ratio:

relatively close (1.96 ± 0.10 ppm for males and 2.66 ± 0.24 ppm for adults) from the reference value: 2.4 mg/g set by Iyengar, V. and Woittiez, J. [19].

The average contents of Pb 26.87 ± 8.03 noted among adults in the study area ppm are more important than children 20.05 ± 1.56 ppm in the same area, and much higher than those calculated in the panel control (0.37 ± 0.07 ppm in children; 0.43 ± 0.04 ppm in adults). Also, it is noteworthy that the average values for the panel studied are quite high compared to the value recommended by Iyengar, V. and Woittiez, J. [19] which is 10 ppm.

Table 2 Average values for MTE in hair samples.

		Cu ppm	Zn ppm	Pb ppm	Cd ppm
Panel C	Children (<i>n</i> = 12)	30.00 ± 8.74	191.08 ± 11.36	20.05 ± 1.56	1.96 ± 0.10
	Adults (<i>n</i> = 50)	38.25 ± 11.14	200.09 ± 13.41	26.87 ± 8.03	2.66 ± 0.24
Panel W [2]	Children (<i>n</i> = 14)	12.87 ± 0.68	96.77 ± 6.93	5.74 ± 0.34	0.37 ± 0.067
	Adults (<i>n</i> = 30)	13.10 ± 1.65	117.40 ± 2.91	5.33 ± 0.12	0.43 ± 0.038

Table 3 PI of MTE in hair samples.

	Cu	Zn	Pb	Cd
Children	2.33	1.97	3.49	5.30
Adults	2.92	1.70	5.04	6.19

Table 4 Average values for MTE in blood samples.

		Cu ppm	Zn ppm	Pb ppm	Cd ppm
Panel C	Children (<i>n</i> = 12)	1819.50 ± 8.87	5820 ± 8	199.27 ± 7.38	1.98 ± 0.085
	Adults (<i>n</i> = 28)	1778.02 ± 21.37	6070 ± 19	210.21 ± 5.40	2.06 ± 0.099
Panel W [2]	Children (<i>n</i> = 36)	716.7 ± 289.9	2100 ± 420	37.40 ± 2.20	0.69 ± 0.45
	Adults (<i>n</i> = 55)	544.8 ± 104.2	2300 ± 330	40.00 ± 4.90	0.71 ± 0.41

The average values in Zn 191.08 ± 11.36 ppm in adults are similar to those of children 200.09 ± 13.41 ppm, and are very high compared with the control panel (children: 96.77 ± 6.93 ppm; adults: 117.40 ± 2.91 ppm).

The same conclusion is repeated for copper.

These values show a strong contamination of the surveyed area.

It appears that these metals are firmly attached to the ground.

The indices of pollution for hair samples reported in Table 3 are for the four metals and assayed for both age groups. It is interesting to note that the PI of adults' hair is larger than those of children.

They reach up to 6.19 for Cd, for Pb 5.04, 2.33 and 1.97 for Cu, with the exception of Zn.

The high values of these PIs can only be explained by a high contamination of the area of study, and also confirm that the adults have the highest index respectively for the two panels, with the exception of zinc which is PI relatively higher among children than 1.97 adults 1.70. In addition, the study of the effect of age on the accumulation of zinc in the hair revealed that there was no significant difference between the average levels of zinc in the hair in children and in

adults ($p < 0.05$).

5.2 Blood Samples

The results are reported in Table 4.

The Cd concentration in the blood observed in adults 2.06 ± 0.10 ppm is relatively higher than that seen in children 1.98 ± 0.08 ppm, and there is a significant difference between topics on the panel studied and those of the witness panel 0.71 ± 0.41 ppm for adults and 0.69 ± 0.45 ppm for children.

Let authors compare with the reference values recorded by Iyengar, V. and Woittiez, J. [19] of the Cd concentrations which are of the order of 0.3 to 0.7 g/dL.

At steady state, the blood lead represents 2% of the amount of lead in the body. Approximately 98% of blood lead is within erythrocytes [20, 21].

The accumulation of this element in blood in the study population was 210.21 ± 5.40 ppm for adults and 199.27 ± 7.38 ppm in children. These average levels noted in the study population seem to be more important as noted in the controls which have respectively 40.00 ± 4.90 ppm and 37.40 ± 2.20 ppm in adults and children. Nevertheless, the average levels recorded in subjects of the panel studied are relatively high compared to the limit value 125 ppm given by

Iyengar, V. and Woittiez, J. [19].

Authors' results show that adults and children in the control panel have average levels of blood zinc (respectively $2,300 \pm 330$ ppm and $2,100 \pm 420$ ppm) less than those in adults and children panel (respectively $6,070 \pm 19$ ppm and $5,820 \pm 8$ ppm).

The zinc reference values in whole blood vary from 6,000 to 7,000 ppm [19].

The average contents of Cu in the panel studied $1,778.02 \pm 21.37$ ppm and $1,819.50 \pm 8.87$ ppm respectively in adults and children are much higher than those noted in the witness panel 544.8 ± 104.2 ppm in adults and 716.7 ± 289.9 ppm in children.

Normal values for Cu in the blood range from 800 to 1,400 ppm [19].

The lead content is subject to many regulatory documents following the environmental conditions. Given the lack of regulations on the limit of lead content in the environment, authors took the example of Canada, which sets 1 ppm the toxicity threshold [22]. The Labour Code concerning the prevention of chemical risk fixed biological limit to 400 ppm.

The cadmium content reference cited by Iyengar, V. and Woittiez, J. [19] in the hair is of the order of 2.4 ppm. The European Directive 15/12/2004 [23] sets 5 ppm limit value of content on health and the environment.

To authors' knowledge, no legal text proposed standard values for the concentrations of Zn and Cu. These two are not supposed to lead to major health risks. It is assumed that Zn becomes toxic at 2 g/d, which is well below the levels measured. In all cases, any excess Zn is offset by a Cu supply. This trace

element is brought in food *via* the Cu pipes [24].

The indices of pollution for blood samples and are reported in Table 5.

6. Comparison of Contamination by MTE from Two Different Sources of Pollution

It seemed interesting to compare the results of contamination by metals trace elements from two different sources of pollution and the operation of the mine site Draa Lasfar located about 10 km West of the city of Marrakech (natural contamination) [2].

The comparison will focus on the content of the four MTE: Cu, Zn, Pb and Cd in blood and hair of two study populations; the comparison item will be the PI pollution indices. *The authors distinguish witnesses' sexes, what people could not do.*

6.1 Hair Samples

The results of analyzes of the contamination in the hair samples by MTE presented in Table 3 are compared with analyzes of pollution from mining (Table 6).

6.2 Blood Samples

The results of analyzes of blood contamination by MTE presented in Table 5 are compared with analyzes of pollution from mining (Table 7).

It is possible to deduce a trend from the examination of these Tables. Whether for hair or blood samples, pollution indices by MTE (except PI Cu blood children) are higher when they are of artificial origin (municipal waste) to the original ones mining. Open landfills, as the uncontrolled discharge

Table 5 PI of MTE for blood samples.

	Cu	Zn	Pb	Cd
Children	2.54	2.77	5.33	2.87
Adults	3.27	2.64	5.26	2.90

Table 6 PI of MTE in hair samples for pollution from mining.

	Cu	Zn	Pb	Cd
Children	1.95-1.83	1.66-1.76	2.61-2.83	5.02-4.57
Adults [2]	2.00-1.96	1.36-1.51	3.63-3.67	4.07-4.78

Table 7 PI of MTE in blood samples for pollution from mining.

	Cu	Zn	Pb	Cd
Children	2.64-3.77	1.61-1.61	5.18-3.58	1.88-2.78
Adults [2]	2.84-2.20	1.74-1.68	4.86-4.51	2.35-2.54

of the city of Marrakech, is removing the main route of any kind of waste. MTE are buried in large quantities and in various forms in these landfills.

The majority of adults are working in the nearby landfill, and they are in constant contact with municipal waste in general including hospital waste, which confronts the assimilation of MTE.

Contamination by waste “outdoors” may be explained in part by:

- climatic characteristics determined by the presence of current that moves the various pollutants to neighboring villages;
- the relationship of the family with the discharge, since all their livestock and poultry feed of this discharge.

7. Conclusion

Landfills are the main route for disposing of domestic, industrial or hospital waste. They can be buried in large quantities and in various forms in these open dumps.

Assessing the impact of solid waste on the health of the population surrounding the uncontrolled discharge of the city of Marrakech has revealed severe contamination of the population via the major MTE analyzed especially Cd which presents quite worrisome levels compared substantive standards and compared to the levels recorded in the control panel. So authors have determined that there is severe contamination of adults of this panel to children of the same panel, and this can only be explained by the fact that the majority of the population works in the nearby landfill as they are in constant contact with household waste in general and hospitals in particular, which confronts the assimilation of MTE.

References

[1] Khan, A., Diffay, B. C., and Mielk, H. W. 1995. “Trace

Elements in Goat Hair.” *Environ. Sciences* 3 (4): 187-92.

[2] Barkouch, Y. 2007. “Study of the Transfer of Trace Metallic Elements (Al, Cd, Cu, Pb Se and Zn) to a Food Chain in a Mining Area in the Marrakech Region—Morocco.” Thesis HDR, Nantes.

[3] Goullé, J. P., Mahieu, L., Castermant, J., Neveu, N., Bonneau, L., Lainé, G., et al. 2005. “Metal and Metalloid Multi-elementary ICP-MS Validation in Whole Blood, Plasma, Urine and Hair. Reference Values.” *Forensic Sci. Int.* 153 (1): 39-44.

[4] Lekouch, N. 2005. “Evaluation of Exposure of Human Population to Metallic Trace Elements in the Marrakech Region: Study of the Mercury Risk.” Thesis HDR, Univ. Cadi Ayyad, Fac. Semlalia, Marrakech, 136.

[5] Gibson, R. S., and Gibson, I. L. 1984. “The Interpretation of Human Hair Trace Element Concentrations.” *Sci. Tot. Environ.* 39 (1-2): 93-101.

[6] Jamall, I. S., and Allen, P. V. 1990. “Use of Hair as an Indicator of Environmental Lead Pollution in Women of Child-bearing Age in Karachi, Pakistan and Bangladesh.” *Bull. Environ. Cont. Toxicol.* 44 (3): 350-6.

[7] Ellis, K. J., Yasumura, S., and Cohn, S. H. 1981. “Hair Cadmium Content: Is It a Biological Indicator of the Body Burden of Cadmium for Occupationally Exposed Worker?” *Amer. J. Ind. Med.* 2 (4): 323-30.

[8] Suzuki, T., Watanade, S., and Matsuo, N. 1989. “Comparison of Hair with Nail as Index Media for Biological Monitoring of Mercury.” *Jpn. J. Ind. Health* 131 (4): 235-8.

[9] Barkouch, Y., Sedki, A., and Pineau, A. 2007. “A New Approach for Understanding Lead Transfer in Agricultural Soil.” *Water, Air and Soil Pollution* 186 (1-4): 3-13.

[10] Yukawa, M., Suzuki-Yasumoto, M., and Tanaka, S. 1984. “The Variation of Trace Element Concentration in Human Hair: The Trace Element Profile in Human Long Hair by Sectional Analysis Using Neutron Activation Analysis.” *Sci. Total Environ.* 38: 41-54.

[11] Pineau, A. 1987. “Contribution to the Study of the Elimination of Trace Elements by the Products of the Secretion of Hair.” Thesis HDR, Nantes: 125.

[12] Cheng, P. C., Saito, S., and Kojima, Y. 1996. “Lead Content in Human Scalp Hair of Rural and Urban Residents in Taiwan.” *Bull. Environ. Contamin. Toxicol.* 57 (6): 952-6.

[13] Miranda, M., Lopez-Alonso, M., Castillo, C., Hernandez, J., and Benedito, J. L. 2004. “Effects of Moderate

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- Pollution on Toxic and Trace Metal Levels in Calves from a Polluted Area of Northern Spain.” *Environment International* 31 (4): 543-8.
- [14] Blanco-Penedo, I., Cruz, J. M., López-Alonso, M., Miranda, M., Castillo, C., Hernández, J., et al. 2006. “Influence of Copper Status on the Accumulation of Toxic and Essential Metals in Cattle.” *Environment International* 32 (7): 901-6.
- [15] Sedki, A. 1995. “Ecotoxicological and Epidemiological Study of the Metallic Contamination of Two Terrestrial Trophic Chains in the Periurban Palm Grove of the Wastewater Treatment Area of the City of Marrakech.” Thèse, Univ. Cadi Ayyad, Fac. Sci. Semlalia, Marrakech: 139 .
- [16] Lekouch, N., Sedki, A., Bouhouch, S., Nejmeddine, A., Pineau, A., and Pihan, J. C. 1999. “Trace Elements in Children’s Hair, as Related Exposure in Water Spreading Field of Marrakech (Morocco).” *Sci. Tot. Environ.* 243: 323-8.
- [17] Sedki, A., Lekouch, N., Gamon, S., and Pineau, A. 2003. “Toxic and Essential Trace Metals in Muscle, Liver and Kidney of Bovines from a Polluted Area of Morocco.” *Science of the Total Environment* 317 (1): 201-5.
- [18] Gellert, W., Hellwich, H., Küstner, H., and Käsner, H. 1975. “Mathematics as a Glance.” *Compendium. VEB Bibliographisches Institute, Leipzig* 28 (2): 828.
- [19] Iyengar, V., and Woittiez, J. 1988. “Trace Elements in Human Chemical Specimens: Evaluation of Literature Data to Identify Reference Values.” *Cli. Chem.* 34 (3): 474-81.
- [20] Clark, M., Royal, J., and Seeler, R. 1998. “Interaction of Iron Deficiency and Lead and Hematologic Findings in Children with Severe Leadind Poisoning.” *Pediatrics* 81: 247-54.
- [21] Cezad, C., and Haguenoer, J. M. 1992. “Toxicology of Lead in Humans.” *Technics and Documentation*. French Documentation Ed. Pari..
- [22] Collective, Decree No. 2003-1254. 2003. “On the Prevention of Chemical Hazards and Amending the Labor Code. ” *Official Journal of the French Republic* 300: 22329.
- [23] Directive, H. A. T. 2005. “Directive 2004/107/EC of the European Parliament and of the Council of 15 December 2004 Rekating to Arsenic, Cadmium, Mercury, Nickel and Polycyclic Aromatic Hydrocarbons in Ambient Air.” *Official Journal L* 23 (26/01): 0003-0016.
- [24] Holford, P. 1997. *The Optimum Nutrition Bible*. Piatkus.