Hydro geochemistry and balance between minerals and solutions in the mercurial zone of Azzaba, North East of Algeria

BENHAMZA Moussa, KHERICI Nacer, PICARD-BONNAUD Françoise¹

Université Badji Mokhtar Annaba - Algérie, Faculté des Sciences de la Terre. Département de Géologie. B.P 12 Annaba 23200 Algérie. Tél., Fax : 038.87.65.62. moussa_benhamza@yahoo.fr

¹ Laboratoire des Sciences de l'Environnement et de l'Aménagement, Faculté des Sciences, Université d'Angers, UFR Sciences, 2 boulevard Lavoisier, Angers Cedex 01 49045, France.

Abstract:

The mercury ore deposit of Azzaba is located on the northern flank of the Limestone Chain, south of Azzaba town, North East Algeria.

The Northern numidian zone is divided in two parts of different litho chemical composition. The Northern part is made of sandstone and clays of Oligocene age, the Southern part is formed by limestones, calcareous micro breccia and carbonated sandstones of the Kabyle ridge (calcareous mountain range).

The different indices of mineralization which outcrop in the kabyle ridge are classified as polymetallics (Pb, Zn, Cu) and mercurial polymetallics (Hg, Pb, Zn, Cu).

Clays and sandstones of the Oligocene present a Hg, Pb, Zn geochemical background contents of respectively 0.6 ppm, 30 ppm, and 60 ppm; on the other hand, the Copper content is relatively high (80 ppm). As for limestones and carbonated sandstones of the ridge, the Hg background contents range from 0.2 to 1.5 ppm; the Cu, Pb and Zn contents are high as well.

In this region, two aquifers were recognized. The Oligocene phreatic aquifer is composed of fissured sandstone alternating with argillaceous layers whereas the deep aquifer is of Paleocene-Eocene age and is made of sandstone, limestone and conglomerate-breccia.

The two aquifers are separated by impermeable clay, microbreccia and limestone of Palaeozoic and Lutetian-Priabonian. The latter is the host of the cinnabar mineralization.

The results of the analyses of nine drilling wells and two springs of both aquifers show three main facies: the bicarbonated calcic, the sulphated calcic and the chlorided magnesian facies

The contamination of the Oligocene aquifer by Hg and Pb is much higher than that of the Paleocne-Eocene.

Thermodynamic interpretation using the simulation of the concentration of the major ions, under the effect of isothermal evaporation (25 °C) by the thermodynamic software "PhreeqC" in terms of balances salt/solution, shows that water of the area is undersaturated compared to halite, leading to its dissolution and the enrichment of water by Na of Cl.

Water is in balance and in some locations is in supersaturation compared to the gypsum and anhydrite, which causes the precipitation of these evaporitic minerals.

The carbonated minerals are supersaturated and tend to precipitate as calcite, aragonite and mainly as dolomite.

Water of the area is undersaturated with $Pb(OH)_2$ and $PbSO_4$, which causes the dissolution of these minerals, resulting in a Pb enrichment.

Water is supersaturated with PbCO₃, which, in the zones of oxidation, causes a precipitation as PbCO₃.

Water is supersaturated compared to $ZnCO_3$ and $Zn(OH)_2$, the consequence of which is the enrichment of water by Zn following the dissolution of these minerals .

Keywords: water, metallic micropolluants, pollution, simulation, model PhreeqC

HYDROGEOCHIMIE ET EQUILIBRE ENTRE MINERAUX ET SOLUTIONS DANS LA ZONE MERCURIELLE DE AZZABA, NORD-EST ALGERIE

Résumé :

Les gisements mercurifères de la zone Nord numidique sont situés sur le flanc Nord de la chaîne calcaire, au Sud de la ville d'Azzaba, Nord-est Algérie.

La zone d'étude est subdivisée en deux parties de composition litho chimique différentes. La partie Nord est constituée de grès et d'argiles Oligocène, la partie Sud est formée par les roches calcaires, les microbrèches calcaires et les grès carbonatés de la dorsale Kabyle (chaîne calcaire).

Les différents indices minéralisés affleurant dans la dorsale kabyle sont classés en poly métalliques (Pb, Zn, Cu) et mercuro poly métalliques (Hg, Pb, Zn, Cu).

Les argiles et les grès de l'Oligocène présentent des teneurs en fond géochimique en Hg, Pb et Zn respectivement de 0.6 ppm, 30 ppm et 60 ppm, par contre la teneur du Cu est relativement élevée (80 ppm). Pour les roches calcaires et les grès carbonatées de la dorsale, les teneurs en fond géochimique du Hg varient de 0.2 à 1.5 ppm ; celles du Cu, Pb et Zn sont aussi élevées.

La zone d'étude est caractérisée par deux nappes aquifères. La nappe phréatique Oligocène composée de grès fissurés alternant avec des lits d'argiles et la nappe profonde Palécène-éocène constituée de grès, de calcaire et des microbrèches calcaires. Ces deux nappes sont séparées par les roches imperméables du Paléozoïque et du lutétien-Priabonien caractérisé par les microbrèches calcaires, les argiles et les calcaires et représentant la minéralisation mercurielle de Cinabre (HgS).

Les résultats d'analyses effectuées sur neuf forages et deux sources situés dans les deux différents aquifères révèlent trois principaux faciès le bicarbonaté calcique, le sulfaté calcique et le bicarbonaté magnésien.

Les eaux de la nappe phréatique Oligocène présentent des teneurs élevées en Hg et en Pb par rapport à celles de la nappe profonde Paléocène-Eocène.

L'interprétation thermodynamique en utilisant la simulation de la concentration des ions majeurs, sous l'effet de l'évaporation isotherme (25 °C) par le logiciel thermodynamique « PhreeqC » en termes d'équilibres sels/solution, montre que les eaux de la région sont sous saturées par rapport à la halite, entraînant la dissolution et l'enrichissement des eaux en Na et en Cl. Les eaux sont en équilibres et par endroits en sursaturation par rapport au gypse et à l'anhydrite, entraînant la précipitation des ces minéraux évaporitiques.

Les minéraux carbonatés se trouvent sursaturés et tendent à se précipiter sous forme de calcite, d'aragonite et particulièrement de dolomie.

Les eaux de la région sont sous saturées en Hydroxyde de Plomb et en sulfates de plomb, ce qui provoque la dissolution de ces minéraux entraînant un enrichissement en Pb. Les eaux sont sursaturées vis à vis du PbCO₃, ce qui provoque dans les zones d'oxydation une précipitation sous forme de bicarbonate de Plomb.

Les eaux sont sursaturées par rapport au ZnCO3 et $Zn(OH)_2$, entraînant la dissolution des ces minéraux et l'enrichissement des eaux en Zn.

Mots Clés : eau, micropolluants métalliques, pollution, simulation, modèle PhreeqC

1. Introduction:

The area of study is located in the North of Algeria on the Northern side of the numidian chain, 30 km away from Skikda and 3 to 10 km from Azzaba (Fig. 1).

The geology of the area is characterized by the presence of two structural groups, one autochthonous and the other allochtonous.

The autochtonous one is composed of deposits of the Kabyle dorsal including formations whose age varies from Trias to upper Eocene. The dislocated deposits of Paleocene are made of sandstones, limestones, micro breccia and breaches are found. The Thanetien-hypresien is made of quartzetic sandstone and limestone and Hyprésien-lutétien is made of conglomerates, limestone micro breccia and sandy limestones. The allochtonous group is formed by a series of rock scales of various age and composition, ranging from metamorphic schists of Paleozoic to clays of Oligocene (Bouarroudj, 1986).

The mercury ore deposits of the district are well located and are gathered in two mining fields. The first field, Ismaïl, is formed by three distinct ore deposits, Ras El Ma, Ismaïl and Guenicha, the horizon carrying the mercurial mineralization are the conglomerates and the limestone micro breccia of Hyprésien-luthétien. The second, Mra-Sma, is formed by Mra-Sma I, MraSma II and koudiat Sma, the carrying horizon of the mineralization being the limestone pseudo breccia of the Campanien and the sandstones of the Neocomien (Bouarroudj, 1986; Mezghache, 1989).



Fig. 1: Location map of the North numidian mercurial zone

The hydrogeology of the area is characterized by two water tables. The Oligocene phreatic water where the aquiferous rocks are the fissured sandstones alternating with beds of clay and the Paleocene Eocene deep confined aquifer, largely developed in the area, and where groundwater is associated to the sandstone, limestone, the conglomerate breccias, fissured cavernous limestones and the calcareous sandstones of the Paleocene.

The two aquifers are separated by impermeable layer of Palaeozoic and Lutetian-Priabonian. The latter are the host rocks of cinnabar mineralization (Benhamza, 1996).

2. Methodology:

Nineteen (19) springs and wells of both water tables were analyzed to identify the major elements (Ca²⁺, Mg²⁺, Na⁺, K⁺, HCO₃⁻, Cl⁻, SO₄²⁻), the pH, the dry residue, the hydrotimetric grade and the mercury content (Table I).

Analyses were carried out at the laboratories of the Petrochemical Complex of Skikda and Boumerdes (Algiers).

The dosing processes are deduced from the methods of standard analyses. Total and calcic hardnesses of the samples are determined by complexometry, by titration with the acid ethylene-diamine-tetracetic (EDTA). The chlorides are determined by the method of Mohr [20] and sulphates by reading the absorbance with λ =420 nm for a suspension obtained by reaction of sulphates with barium chloride. Sodium and potassium are dosed by photometry with flame emission (Telliard, 2002).

The determination of mercury is carried out in two stages. The first consists in oxidizing all kind of mercury in a bivalent state using an acid digestion to obtain elementary mercury. Mercury is extracted by bubbling dry air in the solution. The gas mixture is then sent to the cell of the atomic absorption spectrophotometer without flame.

The concentration of the sample is determined by comparison between the respective absorbance of the sample and the standard solutions. The range calibration is between 0.1 μ g.L⁻¹ and 1.5 μ g.L⁻¹ Hg. The applicability range can be widened by carrying out suitable dilutions (Charlot, 1978, Telliard, 2002).

3. Results and discussions:

3.1 chemical Facies:

The ionic balance error calculated using the results of the chemical analyses is satisfactory (< 5%). The cation - anion ratio is included within the acceptable limits

[0.95 - 1.05], which makes it possible to check the reliability of the analyses and to accept the results (Rodier, 1984).

The representation of the analyses on the Piper diagram (Fig. 2) shows three chemical facies. The bicarbonated calcic one for the Paleocene Eocene water, the chlorided sodic and the sulphated calcic for Oligocene water (Rodier, 1984, Schoeller, 1962).

The bicarbonated calcic facies, the most important, accounting for 95% of the samples is explained by the presence of cavernous limestone and the calcareous sandstone of the Paleocene (Benhamza, 1996, Benhamza, 2005, Benhamza 2007).

The chlorided sodic facies is found in sandy and clayey reservoirs of Oligocene, the chlorides are probably the result of the dissolution of sodium chlorides of the saliferous alluvium. The sulphated calcic facies is located in the sandstones and clays of the Oligocene and is explained by the dissolution of calcium sulphates contained in evaporitic inclusions and the alluvium.

\mathbf{N}_{\circ}	Gisement	Champ minier	Nappe	Désignation	Hd	Résidu sec (mg/l)	TH (° F)	Ca ²⁺ (mg/l)	Mg ²⁺ (mg/l)	Na ⁺ (mg/l)	K ⁺ (mg/l)	HCO ₃ (mg/l)	CI ⁻ (mg/l)	SO4 (mg/l)
1	El Ma	Î	e ¹⁻³	90	6.9	754	45	143	22	110	3.5	450	140	68
2	Ras 1		g ²	S.1	7.8	900	21	32	30	45	5.4	152	90	35
3		Γ	g^2	350	8.0	138	74	222	45	84	17	311	156	505
4	iil	A J	g^2	210	7.0	143	74	208	53	85	19	250	184	524
5	sma	, L	g^2	398	8.9	600	38	50	61	41	35	372	89	37
6	I	5	e ¹⁻³	S.2	7.5	1110	60	165	46	68	5.7	518	53	158
7		Ι	g^2	354	7.5	576	62	120	79	67	10	297	78	104
8	enicha		e ¹⁻³	194	7.0	590	38	50	61	41	3.5	372	89	37
9	Gu	ļ	e ¹⁻³	196	7.0	594	35	88	32	68	3	298	150	45
10	a Sma	a Sma	e ¹⁻³	91	7.8	620	38	104	29	46	1.6	311	120	34
11	Mr	Mrá	e ¹⁻³	93	7.0	820	47	138	31	67	13	300	120	50

Table I: Results of chemical analysis

Désignation	Hg (mg/l)	Cu (mg/l)	Pb (mg/l)	As (mg/l)	Zn (mg/l)
90	0.007	0.003	0.007	0.003	0.07
S.1	0.008	0.008	0.008	0.008	0.08
350	0.08	0.002	0.06	0.02	0.01
210	0.08	0.002	0.06	0.02	0.01
398	0.004	0.002	0.004	0.02	0.04
S.2	0.08	0.002	0.06	0.02	0.01
354	0.08	0.002	0.08	0.02	0.08
194	0.006	0.20	0.03	0.02	0.06
196	0.006	0.30	0.03	0.03	0.06
91	0.006	0.02	0.02	0.02	0.20
93	0.001	0.02	0.02	0.02	0.20



Fig. 2: Representation of the chemical analyses on the Piper diagram

3.4 Mercury contents

3.4.1 Geochemical Characteristics of the Northern numidian zone

Bikmeev studied the geochemical characteristics of the Northern numidian mercurial zone, using samples taken mainly from drill cores and dosed by semi quantitative emission spectrometry. The results show that litho-stratigraphic facies presenting high Hg Clarke are calcareous micro breccia of Thanétien Hyprésien (1.5 ppm), the sandstones and conglomerates of Permo Trias (1.4 ppm), clays and siltites of Luthetien Priabonien (0.9 ppm); whereas the sandstones and clays of Oligocene present low Hg Clarkes (0,6 ppm) (Bikmeev, 1970).

3.4.2 Element migration

The migration coefficient of a given chemical element is defined as the ratio of its average content in water on Clarke of the rock in which this water is circulating.

$$A = (B/C) \times 10^{-4}$$

Where: A= migration coefficient

B = the element average content in water

C = element Clarke in the rock

The results show that the mercury of the Northern numidian mercurial zone presents an average migration coefficient of 0.15 (Table II) (Bikmeev, 1970, Bouarrouidj, 1986).

chemical	number of	Migration	chemical	number of	Migration				
element	drillings	coefficient (A)	element	drillings	coefficient (A)				
S	30	563	Mn	30	0.15				
Cl	30	973	Fe	30	0.007				
Na	29	6.51	Hg	28	0.15				
K	28	0.82	Zn	30	2.56				
Ca	35	5.75	Pb	30	0.11				
Sr	30	5.60	Cu	30	0.31				
SiO ₂	30	0.11							

Table II: Migration coefficient of the North numidian zone [5]

3.4.3 Classification of the elements

The calculation of the migration coefficient makes it possible to classify the elements of the area of study in four groups according to their intensity of migration (Bikmeev, 1970).

This reveals that the calcophile elements Zn and (As-Sb) are more mobile than Hg, Cu, Pb and (Sb-As) (Table III).

Intensity of			oxydiz	ing en	nvironment				
migration	1000	100	10	1		0.1	0.01	0	.001
Very high	Cl - S - Bi	•							
high			Ca - Na -	Mg -					
			Sr- Zn – (A	s-Sb)					
			Mo - U						
medium					Mn - Cu	– Hg -			
					Pb - Sr - I	K - N1 -			
					P - (Sb-A	ls)			
Low and							F 41	т.	
Very low							Fe - Al -	- 11 -	
							Métaux	précieux	

Table III: Supergene migration of the chemical elements in the North numidian zone

3.4.4 Mercury content distribution

The ground water mercury distribution map of the area shows that the high values are situated in the mining field of Ismail. The maximum contents ($80 \ \mu g.L^{-1}$) is located in drillings 350, 210, 354 and the springs S.1 and S.2 of the Oligocene aquifer.

These values are very high according to the standard tolerated for the Hg which is $1\mu g.L^{-1}$ (OMS, 1980). Drillings 94 and 93 collecting the deep Paleocene-Eocene aquifer show a minimal mercury content of $1\mu g.L^{-1}$ (Fig. 3).

The contamination of Oligocene aquifer by the Hg is much higher than that of the Paleocene-Eocene, although the latter contains facies of high Hg Clarke.

Thus this contamination is not the result of leaching of the cinnabar formations, bearing in mind that Hg in the area presents a medium migration coefficient which is less mobile than the chalcophile elements (Benhamza, 1996, Benhamza, 2007, Benhamza, 2008).



Fig. 3: Map of mercury distribution in the North Numidian zone (µg.L⁻¹)

The distribution of mercury in groundwater in the area has thus no relationship with the high Hg Clarke litho-stratigrahic facies. Indeed, the studies carried out in the area showed that the mercury plant contributes to both atmospheric and hydric pollutions.

A part of the mercury contents in water results from recycling of atmospheric Hg by the rainfall, the major part originating from the hydric rejection of the plant (Benhamza, 2005).

The mercury plant has two tanks of decantation not adequate, where the contaminated cooling water of the process are poured. Flooding causes water to overflow the two lakes and reaches the Fendek River which feeds the Oligocene aquifer, whose roof is made of permeable sandy rocks (Benhamza, 1996, Benhamza, 2005, Benhamza, 2007, Benhamza, 2008).

4. State of minerals dissolved in water:

The degree of saturation of water can be estimated by the calculation of the index of saturation, which reaches zero value when the solution is in balance with a solid phase. A positive index of saturation indicates a super saturation and a negative index indicates an under saturation with respect to minerals.

Thermodynamic interpretation by using the simulation of the concentration of the ions major (Cl⁻, SO₄²⁻, HCO₃⁻, Ca²⁺, Mg²⁺, Na⁺ and K⁺), under the effect of isothermal evaporation (25 °C), by the thermodynamic software "PhreeqC" in terms of balances salt/solution, shows that water of the area are under saturated compared to halite (NaCl), which causes a dissolution leading to enrichment of water with sodium and chlorides.

As for gypsum (CaSO₄, $2H_2O$) and anhydrite (CaSO₄), water is supersaturated allowing a precipitation in the form of gypsum and anhydrite. (Fig. 4)



Fig. 4: State of evaporated minerals in water

Water of the area is super saturated in calcite and aragonite in the all the analyzed points, thus leading a precipitation in the form of calcite and aragonite.

Water of the area is super saturated in dolomite in all the analyzed points, thus leading the precipitation of the elements carbonated in the form of dolomite. (Fig. 5)



Fig. 5: State of carbonated minerals in water

Water of the area is under saturated with $Pb(OH)_2$ and $PbSO_4$, which causes a dissolution of these minerals in water involving an enrichment out of Pb. Water is super saturated with respect to $PbCO_3$, which causes a precipitation in the form of Cerusite (PbCO₃). (Fig. 6)



Fig.7: State of Plumb minerals in water

 $Zn(OH)_2$ an $Zn(CO_3)$ are in under saturation, which causes a dissolution of these minerals in water involving an enrichment out of Copper. (Fig. 7)



Fig.7: State of Copper minerals in water

4. Contamination of the population by inorganic mercury

The concentration of mercury in the urines of a non exposed subject is usually of about 0.5 μ g. L⁻¹, although much higher values, never exceeding 25 μ g L⁻¹ has been reported (Buzina, 1989).

A normal subject rejects less than 10 μ g.J⁻¹ in the urines and 10 μ g in excrement (Langworth, 1992).

The issue of pollution by inorganic mercury has been the subject of several studies and publications in the world and in Algeria.

The contamination by the inorganic mercury vapors of the plant workers of Azzaba is well known (Service de toxicologie CHU Mustapha Alger, Service de Médecine du Travail CHU de Annaba - Algérie) (Nezzal, 1994, Benhamza, 2005, Benhamza, 2008).

The average inorganic urinary Hg rate in the workers of the plant mercury of Azzaba varied from 18 to 188 μ g.G⁻¹ of creatinin in 1991 and from 8 to 886 μ g.G⁻¹ in 1993 (Nezzal, 1994).

These results are a clear indication of the mercurial contamination of the plant workers, which at no time was observed on the population leaving around the plant.

In order to check the level of inorganic mercury contamination of the population, a study was carried out by the service médecine de travail du Centre Hospitalo-Universitaire d'Annaba_

The study includes a total of 88 plant workers, 354 school children in the area of Azzaba, around the mercury plant (1 to 7 km) and 124 school children living in the town of Annaba, situated at 80 km East of Azzaba, representing a pilot population.

As for as the choice of age is concerned, half of the population studied is in the first primary year and the second half is in sixth primary year.

The samples consist of a collection of the urines taken in the morning, in a glass tube, filled to the 2/3 to avoid breakings at the time of congelation. The tube is brought back by the children the next morning.

The samples are codified, kept in a freezer before they are carried to the laboratory of industrial toxicology of Sider El-Hadjar (Annaba - Algeria) for analysis, the time between sampling and the analysis not exceeding fifteen days.

The analysis is carried out according to the method of atomic absorption spectrophotometry (cold vapor).

In the biological samples, mercury is related to the thiols grouping, the tin chloride (SnCl₂) added to the samples breaks this bond and reduces mercury to the metal state. The vapors are then transmitted to a cell placed in the beam of an EDL mercury lamp. The absorbance is proportional to the concentration (Nixon, 1996).

The mercury concentration in the urines is corrected according to urinary creatinin.

The method of biological analysis is sensitive to the $1/100 \ \mu g.G^{-1}$ of creatine. The results of the analyses are in table IV.

	Number	min.	Max.	Mean				
plant	88	2	13924	650				
workers								
children of	354	0	17	2.49				
Azzaba								
children of	124	0	4	0.45				
Annaba								

Table IV: Inorganic urinary Hg in creatinin (μ g.G⁻¹) in the plant workers, childrens of Azzaba and Annaba.

The results of the analyses show a high average among the 88 mercury plant workers (650 μ g.G⁻¹ of creatinin); giving a clear evidence of a strong impregnation, the minimum is 2 μ g.G⁻¹ and the maximum 13924 μ g.G⁻¹ of creatinin.

The average in the 124 school children of Annaba is 0.45 μ g.G⁻¹, with a minimum of 0 and a maximum of 4 μ g.G⁻¹, whereas the average observed among the 354 school children living in Azzaba is a 2.49 μ g.G⁻¹ of creatinin, with a minimum of 0 and a maximum of 17 μ g.G⁻¹.

The symptoms of this mercurial contamination (Table V) corresponding to the clinical signs (tremors, writing test, finger nose test), which usually appear only at Hg rates higher than 50 μ g.G⁻¹ of creatinin, are inexistant among the children of Annaba, are observed among those of Azzaba but are conspicious among the factory workers (Lauverys, 1992, Nezzal, 1991, OMS, 1980).

Table V: Clinical signs among the factory workers, the school children of Annaba and Azzaba

clinical signs	children of	children of	Plant workers	
	Annaba	Azzaba	(N = 88)	
	(N = 124)	(N = 354)		
tremors	negative	1.29 %	50 %	
Writing test	negative	0.41 %	50 %	

5. Conclusion

The underground water in the North numidian mercurial zone presents the dominating bicarbonated calcic chemical facies in relation with the hosting rocks of the Paleocene Eocene. The chlorided sodic and sulphated calcic facies result from the composition of the hosting rocks of the Oligocene.

Water of the deep aquifer of Paleocene-eocene range from hard to very hard.

The calculation of the migration coefficients of the chemical elements in the Northern numidic zone showed that mercury has an average migration coefficient of 0.15 as a result of the stability of Cinnabar.

The classification of the elements according to their migration coefficient shows that Hg, Cu, and Pb of the area are less mobile than the chalcophiles elements Zn and (As-Sb).

The limestone and the carbonated sandstone of the dorsal present basic Hg contents varying from 0.9 to 1.5 ppm, whereas the sandstone and the clays of Oligocene have a content of 0.6 ppm.

The high contents of Hg in the analyzed water, up to 80 μ g.L⁻¹, are found in the wells capturing the Oligocene, whereas water of the Paleocene Eocene presents relatively low Hg contents (< 7 μ g.L⁻¹).

The contamination of the phreatic water of Oligocene is thus not the result of the formations presenting a lithostratigraphic facies with high Hg Clarke.

The mercury contents found in groundwater of the area are very high and exceed the standard of $1\mu g.L^{-1}$, showing the contamination of the phreatic aquifer of the Oligocene.

The impregnation by the inorganic mercury of the worker workers is clear. It is weak among the school children of the area of Azzaba but is an actual fact.

The urinary mercury contents among these children are higher than those of Annaba.

The symptoms of this mercurial contamination, appearing usually at inorganic Hg rates higher than 50 μ g.G⁻¹ of creatinin do not exist in the schoolboys of Annaba, are nevertheless observed among those of Azzaba and clearly marked among the plant workers.

The symptoms of mercurial contamination corresponding to the clinical signs (tremors, writing test), which usually appear only at Hg rates higher than 50 μ g.G⁻¹ of creatinin, are inexistant among the children of Annaba, are observed among those of Azzaba but are conspicious among the factory workers.

The mercury norm is largely exceeded in groundwater as well as in population living in the Azzaba region.

Bibliographical references

Benhamza M., 1996. Etude hydrogéologique de la zone mercurielle de Fendek (Azzaba) - Conséquences de l'exploitation des gisements mercuriels sur l'environnement. Thèse de magister de l'université de Annaba, Algérie. 174p.

Benhamza M., 2005. Application de l'Analyse en Composante Principale à l'évolution de la pollution mercurielle dans la région de Azzaba (1999, 2000, 2001). 1er Colloque Euro-Méditerranéen en Biologie Végétale et Environnement, les 28, 29 et 30 Novembre 2005, Université Badji-Mokhtar- Annaba (Algérie). 7p.

Benhamza M., 2007. Contribution de la géophysique à l'étude hydrogéologique de la zone mercurielle Nord Numidique (Azzaba), Nord Est Algérie – Conséquences de l'exploitation des gisements mercuriels sur l'environnement »

Thèse de Doctorat d'état soutenue à l'Université d'Annaba le 16 Décembre 2007

Benhamza M., Kherici N., Piccard-Bonnaud F., Nezzal A.

« Qualité des eaux souterraines de la zone mercurielle Nord-Numidique(Azzaba), Nord – Est Algérie – Evaluation de la contamination de la population par le mercure inorganique ». Bulletin du Service Géologique National, Vol.19, n° 2, pp 1-15, 2008.

Benhamza M., Kherici N, Nezzal A., 2006. Hydrochemistry of groundwater in the mercurial zone Northern numidic (Azzaba), North East Algeria: Evaluation of the mercurial contamination on the population. The third International conference on the « Water Resources in the Mediterranean Basin » Tripoli Lebanon 1-3 November 2006. 5p.

Bikmeev R., 1970. Rapport sur l'étude géochimique, (Rapport E.R.E.M, inédit).

Bouarroudj M.T., 1986. Les minéralisations à Hg, Pb, Zn, Cu, Ba de la zone Nord numidique du Nord de l'Algérie orientale – Métallogénie et recherche de guides de prospection. Thèse de Docteur ingénieur, Université Pierre et Marie Curie, ParisVI. 242p. Buzina R, Subotica, J Vukusic, J Sapunar, K Antonic, 1989. Effects of Industrial Pollution on Seafood Content and Dietary Total and Methyl Mercury: The Science of Total Environemment, 78p, 45-57

Charlot G., 1978.Dosages Absorptiométriques des éléments minéraux. Masson, Paris New York Barcelone Milan. 443p.

Langworth S, Almkvist O, Soderman E, Wikstrom B-O, 1992. Effects of ccupational exposure to central Mercury vapour one the nervous system: British Newspaper of Industrial Medicine, 49p, 545 - 555

Lauverys R., 1992.Toxicologie industrielle et intoxication professionnelle. Ed. Masson.

Mezghache H., 1989. Cartographie automatique et interprétation géostatistique d'une campagne de prospection géochimique sur sol – Application à la zone mercurielle Nord numidique (Algérie). Thèse de Docteur de l'INPL. 178 p.

Nezzal A.M., Gueroui S., Tourab Dj., 1994. L'intoxication chronique au mercure dans la région de Annaba. 3eme Conférence Panafricaine de Santé au travail, Le Caire du 7 au 11 décembre 1994.

Nezzal AM., Nezzal AZ., Gueroui S., Khène M., Ghorab S., Bachtarzi T., 1996. Pollution par le mercure et effets sur la santé des travailleurs et de la population environnante, 10ème JNMT Alger les 7, 8 et 9 Mai 1996.

Nezzal AM, Tourab Dj, Gueroui S, Nezzal AZ, 1991. : Manifestations Neuropsychiques observées au cours de l'intoxication chronique au mercure inorganique : 7ème JNMT Oran 1991

Nixon D.E., Mussman Steam Generator, Moyer T.P, 1996. Inorganic, organic, and total Mercury in blood and urine: cold vapor analysis with automated flow injection sample delivery. Newspaper of analytical toxicology, 20 (1), pp. 17-22.

OMS, 1972. : Normes internationales applicables à l'eau de boisson, Genève.

OMS, 1980. : Exposition aux métaux lourds : Limites Recommandations d'exposition professionnelle ; Rapport d'un groupe de l'OMS.

Rodier J., 1984: Analysis of water; natural water, waste water, sea water, 7eme edition, Ed Dunod, Paris

Schoeller H., 1962. Subsoil waters, dynamic and chemical hydrology, Research, Exploitation and Evaluation of Resources, Masson Edition and Co, Paris 579 p.

Telliard W.A., 2002. Engineering and Analysis Division (4303) U.S Environmental Agency Protection. Method 1631, Revision C: Mercury in toilets by oxidation, Purging and too, and Cold Vapor Atomic Spectrometry fluorescence.