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Study data on Porto Romano inhabitans health from the pollution impact from industrial wastes

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ABSTRACT

Introduction : Porto Romano , a populated area in the 1990s is known for toxic pollution from industrial wastes that persists on the land surface and mainly spread through air , water and food . The main pollutants are monochromate and bichromate of sodium , potassium , followed by organochloric pesticides as hexachloranus and lindane . These toxic pollutants have a significant impact on the health of the inhabitants that lives in the area. Industrial residues of these chemical clusters persist for a period of about 20 years on the surface of Portoromanos , air and water are the main diffusers of the pollution. We are studying the presence of these contaminants in water wells in the area.
Purpose: Extracting the toxicity of groundwater (wells) of the area of Porto Romano and relevant bacterial contamination.
Material and methods: : This study was realized on 2012-2013 period.
To see the action of these contaminants on the health of residents of the area were taken water samples from 17 wells zones.For bacteriological and physico-chemical examinations were taken u analizuan 9 mostra . For chromates and pesticides analysis 17 samples were taken almost from all wells of the area
Results: In the 9 water samples taken for Bacterial examination Bacterial load is seen for: IRM total C and MPNE coli, and in 5 cases bacterial load is seen by IRM Sfaecal. Physico - chemical data of 9 water samples in the area of Porto Romano show that none of the samples complied with the normative indicators allowed.
Also from the results obtained by analyzing water wells for Cr (VI) in 8 of 17 samples the level found was above the allowed values.
In the component examination for lindane was seen his presence in 15 from 17 samples taken for examination.
Conclusions: The above results show that the bacteriological and toxic pollution of water wells in the area have a significant impact on the health of Porto Romano inhabitants as they are still present in the area groundwater.

INTRODUCTION

Porto Romano , a populated area in the 1990s is known for toxic pollution from industrial wastes that persists on the land surface and mainly spread through air , water and food . The main pollutants are monochromate and bichromate of sodium , potassium , followed by organochloric pesticides as hexachloranus and lindane . These toxic pollutants have a significant impact on the health of the inhabitants that lives in the area. Industrial residues of these chemical clusters persist for a period of about 20 years on the surface of Portoromanos , air and water are the main diffusers of the pollution. We are studying the presence of these contaminants in water wells in the area.

There are four main avenue through which pesticides reach the water , they can be stored outside of the target area , can permeate the soil , can be carried in water by flowing or they can be pour in water , for example by accident or negligence of their users .

Pesticides concentracion in water exists in very low levels measured in mg / l . Most pesticides samples fall below the detection limit of current analytical techniques and therefore it is not always appropriate to provide annual data for pesticides .

EU Directive on drinkable water has described thestandards for pesticides in water intended for human consumption . EU parametric values for individual pesticides (0.1 mg / l) and for total pesticides (0.5 mg / l) but not based on any scientific findings . European Union Member States and the European Commission that has approved Drinking Water Directive 98/83/EC believe that pesticides should not be present in drinking water .

Lindane is a white crystalline powder, odorless, tasteless. It is not digested in water but can be dissolved in organic solvents. Lindanecan be found in the form of powder, emulsion, suspension, cream, ect. In practical aspects, now it is known the simple use without combinations with the other pesticides and combined forms of use. Penetration roads on the organism are different (through the digestive apparatus, respiratory route, oral, and through the skin) this depending on their use. The penetration of organochlorines and lindanesthrough the digestive apparatus is doneby eating foods like various vegetables and herbs used by people and animals in their daily food and drinking contaminated water by these pesticides. We will examine the penetration path through the digestive apparatus.

Organochloric Pesticides give an impact on the central nervous system,it is also known that taking repeatedorganochloric insecticides and lindane causes microscopic changes in the structures of liver and kidney, which is proven in experimental animals. One of the properties of pesticides is their storage in adipose tissue. Another special importance is the fact that these substances are still present in meat and especially fat cattle. Lindane is one of the most toxic organochloric preparations, it is about 400-500 times more toxic to insects than to warm -blooded animals, whereas when it is taken by mouth it can cause death in animals in doses of 25-30 mg / kg. Also it is known and proven that lindane is very toxic to humans, so the dose 15-18 mg / kg causes heavy poisoning form up to fatal.

Chromium

Chromium and chromic acid salts have found use in terms of our country's economy. Thus, in Porto Romano sodium and potassiumbichromate are produced for a long period

of time, which are considered the strongest toxic substances. Chromium and chromates have properties so they can be accumulated in the body tissues and organs as for example: in respective endocrine glands (hypophyse), more in the bones and parenhimatose organs and in the bone marrow, in hair, nails and different glands. Chromium salts are held mainly in the plasma proteins. While noting that chromium and chromates have distribution in different tissues and organs and the damages towards them are distributed.

Clinical changes from chromium and its compounds are varied depending on the respective valences, thus: 3-valent chromium is less harmful to the body. It is dangerous to the body if taken in higher doses and when taken for an extended period of time during labor or contact such as environmental toxins, while prolongedenvironmental and professional exposure from 6-valent chromium is associated with disorders of the organs and various systems.

Damages are also observed in the digestive tract where the typical is the development of gastro-intestinal disorders and liver touching, thing that is associated with the development of toxic chronic hepatitis. The relevant person has subicteric coloration on the surface of the skin and sklerat. The liver is increased and become painful during palpation. In the same way change the bilirubin and hepatic tests.

Damages are also observed in the breathing apparatus which is demonstrated by the development of chronic bronchitis in the type of toxic and asmatiform. In the same way may develop pulmonary emphysema and bronchiectasis. Also among the most serious diseases especially 6-valent chromium is the development of lung cancer. It is also known that bichromates and chromates are chemical substances that cause changes in the blood and an increase in the number of leukocytes. They are particularly added polinuclear neutrophils. During chronic forms of poisoning it was observed to be an increase in eusinophiles. A typical factfrom chromium poisoningand its compoundsisthe reduction in the quantity of hemoglobin that occasionally reaches less than 40% of its normal value. It is already known that patients with chronic poisoning by chromium and chromium have anemia of the type of normochromic often hypochromic.

OBJECTIVE

Extracting the toxicity of groundwater (wells) of the area of Porto Romano and relevant bacterial contamination.

MATERIAL AND METHODS

To see the action of these contaminants on the health of residents of the area were taken water samples from 17 wells zones. For getting the water samplesin the beginning were made the selection of the aquatic resources that were mostly close to the landfill and pesticide coverage and also to the former factory area of collection and processing of leather.

For bacteriological and physico-chemical examinations were taken samples only in those cases where the water was used for washing the face, teeth, for cooking or for drinking.

We should note that in the water resources whose water was used for irrigation there were not taken samples for bacteriological and physico-chemical examination but only to see the concentration of pesticides or chromium.
In total, nine samples were taken from water wells that residents claimed that was drinkable. Two of these water wellswere consumed for drinking with consecutive years until the arrival of tap water. Currently the tap water comes with timing and once in three days.
For chromates and pesticides analysis 17 samples were taken almost from all wells of the area. Was expelled any well that was at the same level and distance with the taken samples. Sampling was done by specialists ofPHD(Public Health Department) of Tirana so their analysis and arrival became possible within 2 hours.
Analysis for bacterial load and physico-chemical properties of the samples was done in the laboratory ofPHD (Public Health Department) Tirana.

Methods for determiningthe physical and chemical indicators of taken samples:

Colorimetric Method

This method is based on the water reaction with the appropriate reagents to determine specific indicators. The used equipment for the determination of indicators is spectrophotometer UV-2100. For each indicator a certain wavelength expressed in nm is used. For NH4 analyzing a 420 nmwavelength is used. With this method we can define these indicators: NH4, NO2, NO3, Fe 2 +, Fe 3 +, SO4, P2O5, SiO2.

Volumetric Method

This method is based on the denomination of the solution analyzed in the presence of indicators with corresponding reagents. With this method we can define indicators such as chloride (CI-), HCO3, CO2.

Complexometric Method

This method is based on the cations property to form complex ions for their determination. In this method the appropriate indicators are used and the solution is. In this way it is determined the total hardness expressed in Gj, Ca, Mg.

Kubel's Method

This method is based on the organic matter oxidation with KMnO4 (as strongest oxidizer). In this way the organic matter is defined.
Determination of pH (concentration of H + ions) by the pHmeter.
Determination of electrical conductivity through the conductometer.
Determination of TDS (total dissolved salts) by the TDS meter.

Samples Prelevation Processfor bacterial examination.

Water samples were taken in 500 ml bottles (sterilized in aerosteril in temperature of 180 ° C for 2 hours). Water samples were transported to the laboratory by refrigerator carriers (2-6 ° C), according to the rules of asepsis. The samples were analyzed immediately.

Bacterial loads of analyzed samples is determined by the filtered membrane method and the multiple tubes method.

a. Techniques for determining the Total Coliform

For research and total coliforms counting multiple fermentation tubes method is used. For this is used the field of Mac-Conkei with double concentration, which is divided into tubes with quantity of 10ml and 50ml. In this method the required number of bacteria (total coliform in our case) is calculated by MPN probability tables, or most probable number of bacteria per 100 ml of water.

b. Techniques for determination of Escherichia coli

His determination was made by the filtered membrane method and the multiple tubesmethod. TSA grounds were used for enrichment and ECD as the specific field of detection of Escherichia coli and reactiv indols with the filtered membrane after 24 hours of incubation with the temperature on the thermostat to 44 ° C (Vracko and Scherris).

c. Techniques for determination of faecal Streptococcus

The method used for their determination is the filtered membrane method or the multiple tubes method. A specific ground was used for Enterococci, Slanetz-Bartley Enterecoccus Agar (the composition of which is TTC)

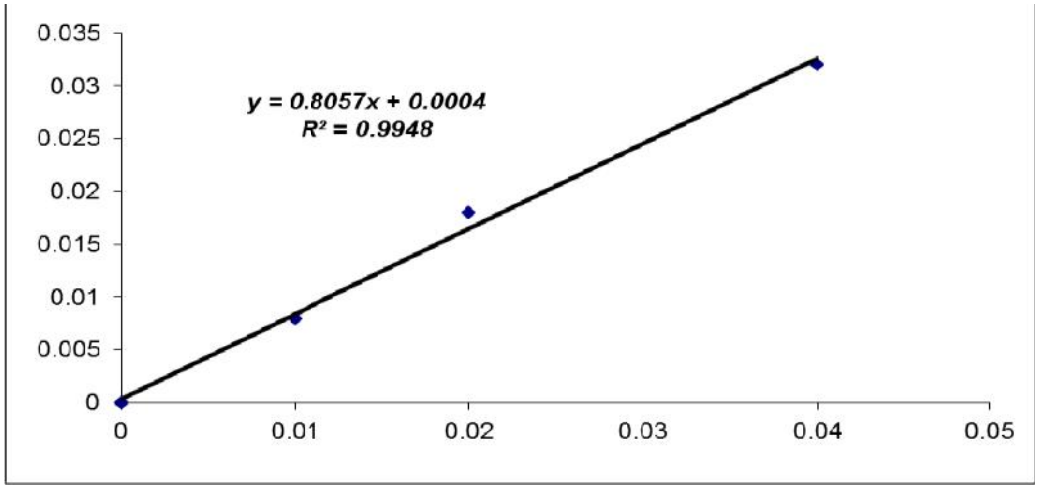
The analysis for pesticides and chromates was done by the laboratory of Analytical Chemistry in Faculty of Sciences Tirana.

Methods for measuring the concentration of Cr (VI) for each sample:

1. Diphenylcarbazide preparation 1%.
2. H_3PO_4 is prepared in the 1:1 ratio.
3. Preparation of the main standard solution 10 mg/L.
4. Preparation of the solution for the calibration curve
   With the balloon 0 the discontinuation of the spectrophotometer is made.With the measured absorbance of the samples 1, 2, 3 the calibration curve is constructed.

Calibration Curve of Cr(VI):

C ppm Cr	**0**	**0.01**	**0.02**	**0.04**
A	**0**	**0.008**	**0.018**	**0.032**



5. Preparation of samples for spectrophotometers measurement.
6. Absorbance measurements were done at 540 nm wave length.
7. Calibration Curve is constructed and the corresponding equation is found.

$$Y = 0.8057x + 0.0004$$

8. From this equation we find the concentration of Cr (VI) for each sample.

Methods for analyzing water samples for the presence of chlorine-organic pesticides:

Extraction and cleaning of chloro-organics from water samples

Water samples were taken on surfaces using Teflon container, suitable for water sampling. Samples were taken at various distances and in different positions to be as representative as possible. Water is passed in glass containers cleaned beforehand. They were kept in cold-temperature -4°C.

For extraction of chlorine-organic pesticides and PCBs from water samples liquid-liquid extraction was used using a separator funnel.

Extraction and cleaning of the sediments samples

Extraction of samples was done in 250 ml Erlenmeyer flask specially prepared and washed well beforehand. In them were thrown milled samples of dried sediment, from 10 grams. It was added TCB internal standard (PCB-29) and the mixture of solvents n-hexane/dichloromethane (30 ml) in the 3:1 ratio. Glass ampules were closed with gas fusion. Extraction was conductedin Bathroom with ultrasound at 30°C for 1 hour. All solvents used in this analysis are of high purity and redistilled in glass.

Extracts were filtered and was passed to Kuderna-Darnish, which was further evaporated to 6-7ml volume. To remove extracted sulfur in the form of mercury sulfide, extracts were treated with methyl mercury. In the sediment samples this action was repeated until the HGS formed.

Further purification of the extract is made by passing it to an open glass column with padding florisil (1 gram). This one was previously extracted with n-Hexane. It was dried at 105°C. Afterwards it was activated in 280°C for 5-6 hours. Then distilled water was added up to 4% and was homogenized. The column was conditioned with hexane and elution of the sample was made with 7 ml mixture hexane/dichloromethane in 4:1 ratio. Emulsion was collected in mini-Kuderna and evaporated up to 1 ml.

GAS CHROMATOGRAPHIC ANALYSIS OF CHLORO-ORGANIC PESTICIDES AND PCB-S

Weinjectedwith a micro syringe, 1 µl of water samplesconcentrate on the apparatus septum HeelPackard 6890. Gas-chromatographicanalysiswasconducted in HP Series II GC-ECDapparatus.

Chromatogramsinjectedinto the Heel Packard Series II 6890 apparatus about the watersamplestaken in Porto Romano are located in the Annex.

METHOD OF CALCULATION OF RESULTS

Calculation of the pollutants concentration in the samples was based on samples chromatograms and standard PCB's and pesticides mixture, injected in same chromatographic conditions, and on the same day. Main calculation parameteris the response factor which is calculated by RF (1):

$$\mathbf{RF = amount\ of\ compound/peak\ area} \qquad \mathbf{(1)}$$

In the same way was calculated the response factor of the TCB internal standard by standard mixing (2):

$$\mathbf{RF_{TCB} = amount\ of\ TCB/peak\ area} \qquad \mathbf{(2)}$$

In the standard mixture chromatogram the RF's values are calculated for all pollutants. On this basis K coefficients are calculated for each of them according to equation (3):

$$\mathbf{K = RF_{compound} / RF_{TCB}} \qquad \mathbf{(3)}$$

The values of the constants K of different pollutants calculated above, was used to compute the concentration in the unknown sample. TCB concentration in the unknown sample was known, because it was added at the beginning of the analysis. Having already known the K coefficients of all compounds and the internal standard concentration in the unknown sample, the compoundsconcentrations in the sample was calculated as follows:

$$\mathbf{Amount\ of\ Comp. = S.\ peak \times K_{comp.} \times RF_{TCB}} \qquad \mathbf{(4)}$$

According to equation (4), the pollutants concentration comes out with the same unit (for exp: ng /g) as the TCB internal standard concentration is expressed.

RESULTS AND DISCUSSION

Some of the results of our study are summarized below

Table 1:Physical and Chemical data of some water samples in the area of Porto Romano

	pH	TDS mg/l	Conductivity µs/cm	Salts %	NH_4 mg/l	NO_2 mg/l	NO_3 mg/l
Sample 1	8.1	436	877	0.05	0.055	0	6.75
Sample2	8.01	394	790	0.05	0.058	0	6.82
Sample3	7.46	3200	6400	0.4	0.27	0	7.27
Sample4	7.61	1950	3910	0.24	0.21	0.024	9.702
Sample5	7.21	1757	3510	0.21	0.16	0.029	6.93
Sample6	7.14	2100	4170	0.25	0.148	0.026	7.48
Sample7	7.39	1400	2790	0.17	0.138	0.024	6.23
Sample8	7.88	403	806	0.05	0.05	0	6.58
Sample9	7.46	1023	2040	0.12	0.064	0.025	15.14
Rate Drinkable Water	**6.8 -8,5**	**700 - 1200**	**400**	**0.05**	**0 -0.05**	**0 -0.05**	**25 - 45**

TDS - General mineralization; Conductivity - electrical conductivity

Sample1 rr. 5 Shkurti(1)
Sample2 rr. 5 Shkurti(2)
Sample3 rr. Begas
Sample4 rr. Metropolitia(1)
Sample5 rr. Metropolitia(2)
Sample6 rr. Metropolitia(3)
Sample7 rr. Metropolitia(4)
Sample8 Rruga e Arbrit
Sample 9 Shkolla Met Hasa

Microbiological data in some water samples in the area of Porto Romano

Table 2: Water samples datato see the bacterial load.

	MPN C total	**MPN Ecoli**	**MPN Sfaecal**
Sample 1	5	2	0
Sample 2	9	5	0
Sample3	More than 16	9	2
Sample4	16	9	2
Sample5	More than 16	More than 16	9
Sample6	5	5	0

Sample 7	More than 16	More than 16	9
Sample 8	2	2	0
Sample9	More than 16	More than 16	9
Rate Drinkable Water	**0**	**0**	**0**

MPN - the most probable number
As is seen from the above table in all water samples taken for examination Bacterial load is noticed.

Cr (VI) water analysis of samples taken from wells in the area of Porto Romano with difenylkarbazid.

Table 3:Presentation of the findings results of component Cr (VI).

Nr	Samples	Quantity of Cr (VI) µg/L
1	A. Goga 10	9.5
2	Rr. Metropolis 6	32.2
3	Rr. Metropolis 7	32.2
4	Rr. Metropolis 4	9.5
5	A. Goga 14	1.24
6	Rr. Pegaso 3	17.8
7	Shkolla Met Hasa 9	< 0.5 (standard limit)
8	Rr. Metropolis 5	7.44
9	A. Goga 13	< 0.5 (standard limit)
10	Rr. 5 Shkurti 2	< 0.5 (standard limit)
11	Rr. 5 Shkurti 1	< 0.5 (standard limit)
12	A. Goga 11	< 0.5 (standard limit)
13	Rr. Arberit 8	< 0.5 (standard limit)
14	A. Goga 12	38.4
15	Rr. 5 Shkurti	< 0.5 (standard limit)
16	A. Goga 15	< 0.5 (standard limit)

As seen from the above table in 8 of taken samples the amount of Cr (VI) is above the permitted water rates.
Samples water analysis taken in the wells area of Porto Romano for the presence of chlorino-organic pesticides.

Table 4:Presentation of the findings results of lindane component.

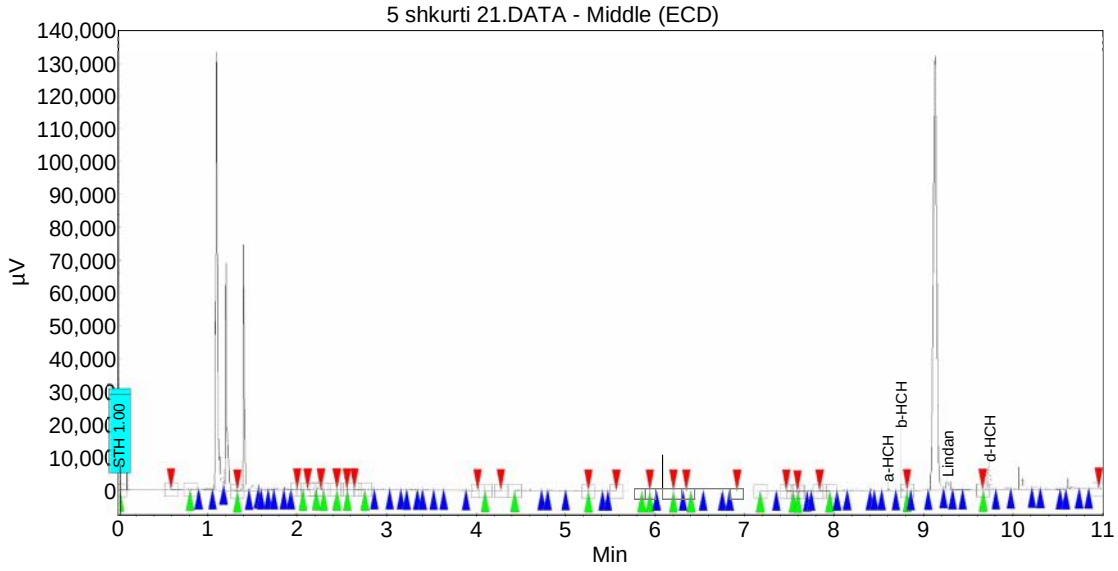
Sample Nr---	**Address**	**Result (**µg/L**)**
1	Rruga 5 shkurti 2	0,10
2	Pegaso 2	0,04
3	Metropolia 7	0,04
4	Metropolia 4	0,08
5	A.Goga 12,1	0,13
6	A.goga 12,2	0,53
7	Metropolia 5	0,01
8	Pegaso 1	0,04
9	A.Goga 15	0
10	A.Goga 11	4,02
11	A.Goga 13	0,04
12	A.Goga 14	0,25
13	Ali kondeli	0,05
14	5 shkurti 1	0,15
15	Metropolia 5	0
16	Metropolia 6	0,02
17	Kuvendi I Arberit	0,09

More detailed data are provided in the following chromatogram:

Chromatogram : 5 shkurti 21_channel1

System : SystemLAO
Method : lindane
User : lao

Acquired : 7/16/2013 9:46:20 AM
Processed : 7/16/2013 9:57:26 AM
Printed : 7/17/2013 7:13:07 AM



Peak results :

Index	Name	Time [Min]	Height [µV]	Area [µV.Min]	Quantity [pg/g]
57	a-HCH	8.60	513.9	30.4	0.00
58	b-HCH	8.75	513.5	26.5	0.00
62	Lindan	9.27	2671.9	133.1	0.10
65	d-HCH	9.74	6953.0	304.3	0.00
Total			449370.6	13469.6	0.10

As seen from the above table in the 9 water samples taken for Bacterial examination Bacterial load is seen from: IRM total C and MPNE coli, and in 5 cases bacterial load is seen by IRM Sfaecal.Physico - chemical data of 9 water samplesin the area of Porto Romano show that none of the samples complied with the normative indicators allowed. Also from the results obtained by analyzing water wells for Cr (VI) in 8 of 17 samples the level found was above the allowed values.
In the component examination for lindane was seen his presence in 15 from 17 samples taken for examination.

CONCLUSIONS

The above results show that the bacteriological and toxic pollution of water wells in the area have a significant impact on the health of Porto Romano inhabitants as they are still present in the area groundwater.

Recommendations: Wells water on this area should not be used for drinking, body washing, fruits and vegetables washing, and also should not be used for irrigation. For thispopulation awarenessshould be madefor the damages on thehealth through the health personnels or informational assets as newspapers, news ect. Local officials inform on the current state of the water wells in order to make possible a drinkable water supply consistently and without interruption.

Acknowledgments
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Annex III (Web-side)

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