EVALUATION OF HUMAN EXPOSURE TO HEXACHLOROBENZENE AT SAMARITÁ, SÃO VICENTE, SÃO PAULO, BRAZIL

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In the Samaritá area of São Vicente city, São Paulo State, Brazil, a chemical industry discarded for several years, with no environmental protection, a mixture of residues containing 55 to 85% of hexachlorobenzene (HCB) and others in smaller quantities. In order to evaluate the impact of these residues on the health of the local population, blood serum samples taken from 234 people dwelling at several quarters of this area for over two years were analyzed, divided into 6 sectors: A - Quarentenário and neighborhood of the industrial wastes dump at 67-km; B - Jardim Rio Branco; C - Parque das Bandeiras; D - Gleba II; E -Vila Samaritá; F -Vila Ema, Vila Iolanda, Vila Mathias. Ten blood samples from residents of an area considered no exposed from Itanhaém city were collected to provide baseline information and HCB was not found in any of the samples. HCB residues were analysed by gas chromatography with an electron capture detector, with a determination limit of 0.02 μg/dL. The mean of HCB in blood serum for the inhabitants of the affected area presented significant differences ($p < 0.001$) between sector A (0.41 μg/dL) and all the others sectors: B (0.04 μg/dL); C (0.04 μg/dL); D (0.03 μg/dL); E (0.04 μg/dL): F (0.04 μg/dL). Although it has not yet been possible to correlate such findings with the presence of diseases among the area inhabitants, this study indicates that the HCB residues are a health risk, as they not only contaminate the environment, but are also present at the biota, including humans.

KEY-WORDS: INDUSTRIAL CHEMICAL RESIDUES; HEXACLOROBENZENE; ENVIRONMENT - CONTAMINATION.

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1 INTRODUCTION

Samaritá is located in the mainland area of the São Vicente Municipality and has 69 km^2 of area bordering Cubatão and Praia Grande Municipalities at southern seacoast of São Paulo State (Brazil). This is a sea level area, relatively inhabited, crossed by two major rivers, Rio Branco and Rio Mariana, both affected by the sea tides. The Barreiros channel of salt water separates the mainland area from insular part. An estimated 12.000 tons of chemical waste were disposed near to urban areas, close to rivers or streams and to mangrove areas and had percolated through the soil.

Most part of this hazardous waste is located in Samaritá region (Figure 1 - Samaritá map and the organochloride residues dumpsites). According to the polluter industry, residues are composed basically of 55.0 to 85.0% of hexachlorobenzene (HCB), the major formed product of the synthesis of pentachlorophenol, percloroethylene and carbon tetrachloride; 20.0 to 35.0% hexachlorobutadiene (HCBD), 0.5% carbon tetrachloride, 0.5% perchloroethylene, 0.5% hexachloroetane; tetrachlorobenzene, pentachlorobenzene, chloroform, are also present but in smaller quantities (RHODIA, 1985). The Environmental Agency for the State of São Paulo, Cetesb, also found 0.2 to 3,6% of pentachlorophenol (MESQUITA, 1995).

HCB is an organochlorinated compound that accumulates in living beings, in fat tissues, in the liver, kidneys, pancreas and central nerve system, and may be found even years after the exposure. (ATSDR, 1997; COURTNEY,1979; EPA, 1988; MORRIS & CABRAL, 1985; UNIVERSITAT DE BARCELONA, 1988).

It has a worldwide distribution due to its use as a fungicide for treatment of seeds and also as common contaminant of some pesticides like pentachloronitrobenzene (MORRIS & CABRAL, 1985) and by-product of some chemical industrial processes, what happens on this particular study case. HCB is not commonly found in Brazilian environment, which makes the compound a good biomarker of exposure to these residues. Its use was restricted and it is forbidden for any practice in Brazil since 1989, Law 7802/89 (BRASIL, 1989). Also, it is not usual to find it in milk or any kind of food, like it happens with DDT or HCH, pesticides, frequently found in any research of the country (BERETTA & DICK, 1989; COSTA et al., 1993; LARA et al, 1982; LARA et al., 1985; OPAS/OMS, 1988; WILLRICH & DICK, 1989).

Moreover, HCB has bio-magnifying characteristics, i.e., the higher the place of a living being in food chain, the greater may be its HCB levels, and therefore it constitutes a problem to the public health (ATSDR, 1997;

COURTENEY, 1979; EPA, 1988; OIT, 1983; KOSS,1978; MORRIS & CABRAL, 1985; UNIVERSITAT DE BARCELONA, 1988). HCB has been related to some serious pathological cases in humans, such as Porphyria Cutanea Tarda and there are also clear evidence, at the experimental level, of its carcinogenic effects on some species. (ATSDR, 1997; COURTENEY, 1979; EPA, 1988; OIT, 1983; KOSS, 1978; HARDELL, 1985; UNIVERSITAT DE BARCELONA, 1988).

HCB was a major compound of the chemical waste in Samaritá representing 16% of the total weight in report published by Cetesb (MESQUITA, 1995). An affluent of Rio Branco (km 69) had HCB levels between 0.9 to 4.2 μg/L and water from the swamp area (km 67) between 0.3 to 6.2 μg/L. Two wells at Parque das Bandeiras sector had 28 and 42 μg/L of HCH respectively (MESQUITA, 1995).

During 1986 water samples taken from wells at 25 points within that region were analysed (MESQUITA, 1995). Among them, 9 (36.0%) showed HCB levels above the values recommended by OPAS (1987) which is 0.01 μg/L. The highest value found was 0.19 μg/L (MESQUITA, 1995).

In 1987, HCB was quantified at the surface of the Quarentenário industrial waste dumpsite at levels varying from 342 to 815 mg/kg. In the marshy area near it, such levels ranged from 54.4 to 122.0 mg/kg and at the deep strata of the soil the levels were between 111 and 570 mg/kg (MESQUITA, 1995).

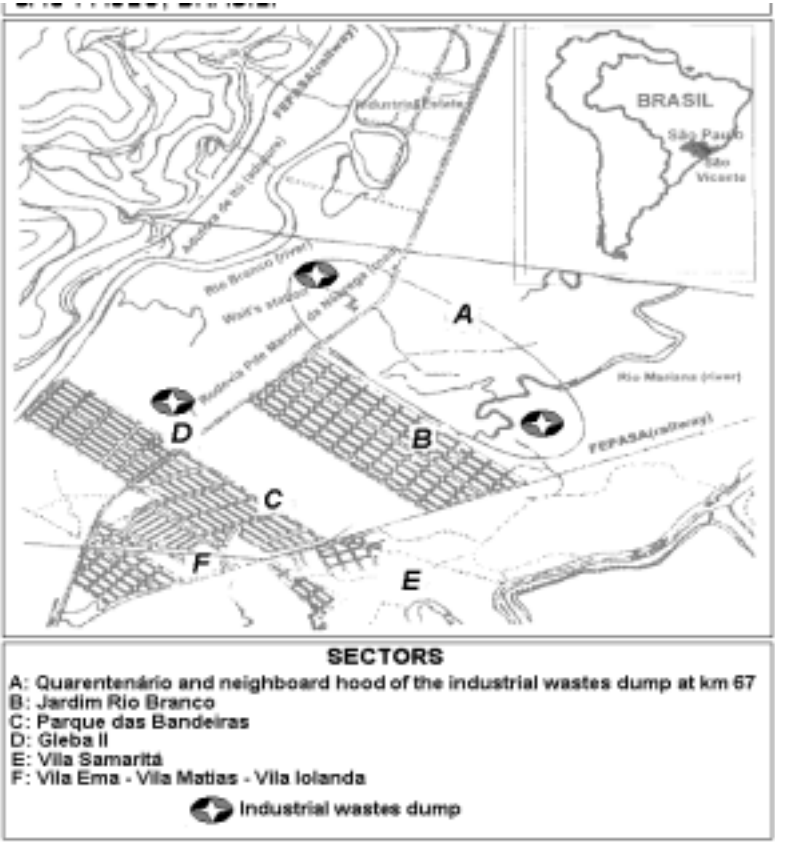
BERNARDES & CLEARY (1988) marked ten points from the waste dumpsite up to the dwelling in the Quarentenário quarter. At these points the HCB levels evaluated in the well water ranged from < 0.06 to 6.70 μg/L; in the soils, these levels oscillated between 1.1 and 325 μg/kg.

At the beginning of 1988 analysis performed by Cetesb for some aquatic specimen from Samaritá showed HCB levels between 0.6 and 23.6 μg/kg (MESQUITA, 1995).

In response to a request from Samarita's inhabitants, in 1987, São Paulo Secretary of Health began to work with the problem setting up a multi-speciality task group to co-ordinate the monitoring process and evaluate the impact for health. The data exposed here are a part of this work.

The first objective was to find out whether the people living close to the hazardous waste sites were actually exposed to the residues and what could be the possible pathways to the body burden. Also, if there could be a gradient on the HCB levels according to distance of the residence from the waste sites. Differences in age and sex were of interest for they could eventually explain differences between sectors.

FIGURE 1 - LOCALIZATION OF STUDIED SECTORS AND INDUSTRIAL WASTES DUMP IN SAMARITÁ, SÃO VICENTE, SÃO PAULO, BRASIL



2 MATERIALS AND METHODS

The area was subdivided in six sectors, in accordance to natural borders and their record of soil occupation (Figure 1).

The maps were based on sketches drawn by local enterprises, on information provided by the São Vicente Municipal Administration and on reports of aerial photography surveys. The population distribution pyramid for the São Vicente Municipality, given by IBGE (1988) was employed for

the inferences regarding population developments.

A rapid count of dwellings was performed at the area, which were numerated in clockwise direction and the houses were then selected by lot. After personal interview where the people were invited to participate in the research, they were classified by sex and age, frequency of consumption of well water, consume of fish, crabs, prawn and vegetables produced at the region and also, time of residence in the area.

To provide baseline information 10 samples of blood serum were collected from people not exposed dwelling in Itanhaém Municipality (five men and five women), whose data in regard to time of residence, age distribution and others were similar to those of the Samaritá population.

Then, 234 blood samples, 102 men and 132 women, were collected from people with age > 15 years old, that has been dwelling for over 2 years in the area, constituting the exposure group. The samples were transferred to glass tubes with caps, which were then kept. The whole blood sample was placed in the refrigerator for about 30 minutes for a setting period and then centrifuged for sufficient time for the separation of at least 3 mL of clear blood serum. This serum were packed on dry ice and transported in refrigerated box to the laboratory where they have been maintained at 2-5 ^{o}C for period up to 24 hours before analysis. The method for determination of the levels of Hexaclorobenzene was previously described by DALE & MILES (1970): 1 mL aliquots of blood serum is extract two times with 5 mL of n-hexane for 1 min on a speed rotator mixer. The extracts are concentrated in a Nitrogen atmosphere with water bath at temperature of 45 ^{o}C and the final volume is adjusted to 1 mL. A suitable aliquot is analysed by gas chromatography equipped with electron capture and splitless injector and 1.5% OV 17 + 1.95% OV210 in Chromosorb QII, 100-120 mesh packed column. The operation conditions were oven, injector and detector temperatures, 210 ^{o}C, 220 ^{o}C and 230 ^{o}C respectively. The carrier gas was 40 mL/min of Nitrogen (high purity grade). Limit of determination was 0.02 μg/dL for Hexaclorobenzene. The results are reported on a blood serum are not correct for recoveries that were 85.8%. The accuracy of method was 7.2.

For the quantitative variables it was applied the variance analysis ANOVA with 1 factor for the six studied sectors (WEISS, 1993). For qualitative variables Chi - square was used. The risk level was evaluated taking into account the set of correlated information (WEISS, 1993).

2.1 QUALITY CONTROL

All standards and stock solutions are checked for purity, accuracy,

storage, stability, etc. according to the rules established in the Quality manual of the laboratory. During routine CG analysis, a standard control prepared freshly each day is always included in the samples series. The laboratory has participated in inter-laboratory check quality control every year.

3 RESULTS AND DISCUSSION

A total of 234 people were submitted to the exam, being 102 men (43,59%) and 132 women (56,41%), they were distributed through the following sectors as shown in Table 1.

TABLE 1 - POPULATION DISTRIBUTION ACCORDING TO SEX AND AGE (YEARS)

Sector	Masculine	Feminine	Total	Age mean (years)
A	5	9	14	30.7
B	32	36	68	36.6
C	39	59	98	35.3
D	9	8	17	31.4
E	7	6	13	42.9
F	10	14	24	33.7
Total	**102**	**132**	**234**	**35.4**

Chi-square = 2.456 fd = 5 Probability = 0.7830 (sex)

Source of variation (age)	fd	Σ Square	Mean Square	F Observed	p
Between sectors	5	1478.986	295.797	1.530	0.1813
Residue	229	43883.632	193.920		
Total	**234**	**45362.618**			

Fd = degrees of freedom; F = factor; p = proportion.

No significant differences between sex distribution among sectors were found. Variance analysis was applied for age distribution and no difference among sectors was found.

For the quantitative variable HCB level, the mean levels for the six sectors studied were compared using variance analysis - ANOVA (WEISS, 1993). The results obtained are shown in Table 2.

TABLE 2 - HCB LEVELS IN THE SAMARITÁ POPULATION

Sector	Quarters	Number of samples	Mean (µg/dL)	Median (µg/dL)	Range (µg/dL)
A	QuarentenÆio and neighborhood of wastes dump at km 67	14	0.41 ± 0.52	0.19	0.02 - 1.78
B	Jardim Rio Branco	68	0.04 ± 0.02	0.05	0.02 - 0.09
C	Parque das Bandeiras	98	0.04 ± 0.03	0.05	0.02 - 0.25
D	Gleba II	17	0.03 ± 0.01	0.02	0.02 - 0.05
E	Vila SamaritÆ	13	0.04 ± 0.02	0.05	0.02 - 0.07
F	V.Ema, V.Iolanda, V. Mathias	24	0.04 ± 0.01	0.02	0.02 - 0.05

Source of variation	Fd	∑squares	Mean Square	F Observed	p
Between sectors	5	181.248	36.250	22.915	< 0.001
Residue	229	362.499	1.517		
TOTAL	**234**	**543.509**			

Source of variation	Fd	∑ Squares	Mean Square	F Observed	P
Between sectors	4	0.107	0.027	0.592	0.6684
Residue	216	9.783	0.045		
TOTAL	**220**	**9.890**	**5**		

Fd = degrees of freedom; F = factor; p = proportion.

The results show a significant difference between the mean value for the A sector and those of the other sectors ($p < 0.001$) as shown below through variance analysis. For the later, differences among mean values are non-significant. The median value for Sector A was 4 times higher than others. Taking out Sector A, the differences started to be of no statistic significance.

The results of the survey about the consumption frequency of well water and of local food from the region can be seen in Table 3. The person interviewed was considered a consumer whenever he had ingested for some time local water from wells and food articles. These variables were mapped in order to detect possible routes of exposure from the residue dumpsites.

TABLE 3 - CONSUMPTION FREQUENCY OF WELL WATER AND LOCAL FOOD BY THE SECTOR INHABITANTS

Sector	Well-water consumption (%)	Local food consumption (%)
A	100.0	72.7
B	75.0	48.5
C	40.8	42.9
D	11.8	23.5
E	7.7	69.2
F	75.0	29.2
Total	**53.8**	**44.5**
Chi-Square	58.517	14.384
Fd	5	5
Probability	< 0.001	0.0132

Fd = degrees of freedom.

The results showed significant differences between the sectors ($p < 0.001$ and $p < 0.05$, respectively). It should be noted that the A sector inhabitants are those with higher consumption levels for well water and local food.

Time of residence (Table 4), was compared among sectors and an important difference between sector E and the others appears to be significant, as it is the most antique sector of the region.

Taking out Sector D (new sector) and E (the former), which had respectively, 2 and 19 years of residence, differences disappeared.

HCB levels in the blood samples of the exposed area inhabitants presented a significant difference between A sector and all other sectors ($p < 0.001$).

The exposure intensity is very different. Sector A inhabitants have mean HCB levels ten times higher than elsewhere in the area. Sector A is the only one not provided with a drinking water supply system, its inhabitants use continually water taken from wells and there are no natural barriers to impede or difficult access to that area even though the number of inhabitants is continuously growing.

Control samples from Itanhaém did not present detectable residues of HCB.

TABLE 4 - TIME OF RESIDENCE IN SAMARITÁ (YEARS)

Sectors	N	mean observed
A	11	6.182
B	68	8.956
C	95	8.768
D	17	2.000
E	12	19.000
F	22	6.955

Source of variation	Fd	∑ Squares	Mean Square	F Observed	p
Between sectors	5	2173.192	434.638	13.260	<0.001
Residue	219	7178.364	32.778		
TOTAL	224	9351.556			

Source of variation	Fd	∑ Squares	Square mean	F Observed	p
Between sectors	3	132.590	44.197	1.764	0.154
Residue	192	4810.364	25.054		
TOTAL	195	4942.954			

Fd = degrees of freedom; F = factor; p = proportion.
N = number of samples.

4 CONCLUSION

As there is no value that may be considered as a threshold for natural levels, the presence in the human body of these residues is considered undesirable in whatever level. Although it has been not yet possible to correlate these residues with diseases among the population, the present study is conclusive enough to demonstrate that the HCB in Samaritá is a problem for human health because, besides polluting the environment, it is also found in living beings, including humans.

There is need of control measures with priority centered on protecting the population's health, keeping the environmental conditions under permanent monitoring, as well as expanding the water supply and sanitation systems to cover the whole area.

New researches for diagnosing and following up the health conditions of that population are indispensable.

Following up the HCB levels in the population may be used as a parameter for evaluating the evolution of exposure conditions to the industrial waste dumps, although it should not be employed as the only parameter.

The local population should be informed, and the work of all agencies and segments involved have to be combined to ensure a joint coordinated action.

Resumo

AVALIAÇÃO DA EXPOSIÇÃO HUMANA AO HEXACLOROBENZENO EM SAMARITÁ, SÃO VICENTE, SÃO PAULO, BRASIL

Na área de Samaritá, cidade de São Vicente, São Paulo, Brasil, resíduos químicos industriais foram descartados por vários anos, sem proteção ambiental, contendo 55 a 85% de hexaclorobenzeno (HCB) e outros produtos em menores quantidades. Para avaliar o impacto à saúde foram analisados soro sangüíneo de 234 pessoas de diversos bairros da região, com mais de 2 anos de residência, subdivididos em 6 setores: A - Quarentenário e vizinhança do lixo industrial a 67 km; B - Jardim Rio Branco; C - Parque das Bandeiras; D - Gleba II; E - Vila Samaritá; F - Vila Ema, Vila Iolanda, Vila Mathias. Dez amostras de soro sangüíneo de habitantes de Itanhaém, área considerada não exposta, foram coletados para fornecer dados de referência. HCB não foi encontrado em nenhuma destas amostras. Resíduos de HCB foram analisados por cromatografia a gás com detetor de captura de elétrons e limite de determinação de 0,02 μg/dL. Os níveis médios de HCB no soro sanguíneo dos moradores mostraram-se significativamente diferentes ($p < 0.001$) entre o setor A (0.41μg/dL) e os demais setores: B (0.04 μg/dL); C (0.04 μg/dL); D (0.03 μg/dL); E (0.04 μg/dL): F (0.04 μg/dL). Ainda que não seja possível estabelecer correlações com doenças encontradas na população, este estudo demonstra que os resíduos de HCB constituem problema para a saúde, pois além de contaminar o meio ambiente são encontrados em seres vivos, inclusive no ser humano.

PALAVRAS-CHAVE: RESÍDUOS QUÍMICOS INDUSTRIAIS; HEXACLOROBENZENO; MEIO AMBIENTE - CONTAMINAÇÃO.

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