

MONITORING OF PERSISTENT ORGANIC POLLUTANTS: WATER RESERVOIRS OF ARMENIA

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Monitoring studies were performed to examine the content of Persistent Organic Pollutants (POPs): DDT, HCH, Lindane, Hexachlorbenzene, and Heptachlor in water reservoirs of the Republic of Armenia. Our findings demonstrated that the levels of DDT, HCH (α and β) and lindane significantly decreased in water samples as compared to previous years. In some particular cases DDT and HCH were not determined. Detection of DDT and HCH in water samples allows concluding that these pesticides continue to be illegally applied by private owners at some agricultural farms. The amounts of Heptachlor and Hexachlorbenzene revealed in samples of water result from activity of some industrial enterprises and processes at which PCBs and Hexachlorbenzene are used or generated.

In Armenia already in late 1960s the problem of environmental pollution arose, as organochlorine pesticides were widely used. The reason for their large-scale application was conditioned by general versatility of these preparations. Many of them possessed acaricidal, insecticidal and fungicidal properties. It was stated that both by the quantities applied and by the assortment (taking into account the formulations as well), organochlorine pesticides took the first place amongst all other pesticides, not to take into consideration such traditionally used substances as slaked lime, copper sulfate (blue vitriol) and compounds of sulfur.

The load of organochlorine pesticides per 1 hectare of arable land made 8.4 kg in the Republic of Armenia, while the load of organochlorine pesticides per capita made 1.72 kg. In the region of Ararat valley these values achieved 21.1 kg and 5.3 kg, appropriately.

As a result of survey performed in 1960s by the sanitary service of Armenia it was revealed that such organochlorine pesticides as DDT and HCH, including Lindane (β -HCH), were found in samples of food-stuffs, especially those of animal origin, and in samples of water from open reservoirs. The level of residual amounts, as well as the percent of determination was high. There was an evident pollution of soil and open water reservoirs.

Assessment of environmental pollution was done through monitoring of organochlorine pesticides (table 1).

Table 1. DDT and HCH in some water reservoirs, Armenia, 1970 (in mg/l)

| Water Sources | Pesticides | Average content in samples | Exceeding MAC, % | Exceeding MAC in some regions |
|---|------------|----------------------------|------------------|-------------------------------|
| rivers, lakes, water reservoirs, channels | DDT+ DDE | 0.021±0.055 | 26.6 | 50-60 |
| | HCH | 0.01±0.025 | not revealed | - |
| artesian wells | DDT+ DDE | 0.11±0.05 0.07±0.04 | - | - |

In 1968-1970 monitoring study involved analyses of 269 samples of water from open water reservoirs. Findings obtained as a result of these studies were considered as background information for the assessment and evaluation of the current state of environmental pollution by POPs in the Republic of Armenia.

Statistic data signify to the fact that DDT and HCH in samples of water from open reservoirs made correspondingly 61% and 24.7 %.

The content of DDT and HCH in samples from water reservoirs made 0.021 mg/l and 0.01 mg/l, in water samples from artesian wells the content achieved 0.11 mg/l and 0.07 mg/l, appropriately. At those years studies were performed in different regions of the Soviet Union in order to determine the level of pollution by organochlorine pesticides in various environmental objects/ media. The results thus obtained became the basis for decision making on prohibition to use DDT as a pesticide in the agriculture of the USSR already in 1970.

Since 1980 the sphere of HCH application for prevention and fight against pests and diseases of food crops was narrowed. The decision was made banning to apply HCH in the region of storage basin of Sevan Lake since 1980.

Studies on DDT and HCH content in samples of water, silt/sludge and muscle tissues of fish from Sevan Lake after the above-mentioned action revealed that on the average DDT and HCH were found in waters of Sevan at 0.0004 mg/l (Small Sevan) and 0.0003 mg/l in Bigger Sevan (Table 2).

Table 2. Pesticides Average Content in water of Sevan Lake and the rivers flowing into Sevan, 1980 (in mg/l)

| Water reservoir | % of determination | DDT | % of determination | DDE | % of determination | HCH |
|---------------------|--------------------|------------------|--------------------|------------------|--------------------|-----------------|
| Small Sevan | 92.3 | 0.0004 ± 0.00007 | 30.8 | 0.00000021 ± - | 100 | 0.0028± 0.0017 |
| Bigger Sevan | 92.7 | 0.0028 ± 0.0024 | 50 | 0.0001 ± 0.00007 | 100 | 0.0034 ± 0.0016 |
| Masrik river | 100 | 0.005 ± 0.004 | 40 | 0.0002 ± 0.00017 | 100 | 0.0034 ± 0.002 |
| Gavaraget river | 80 | 0.0005± 0.0001 | 20 | 0.00004 ± - | 100 | 0.0024 ± 0.0004 |
| Argichi river | 75 | 0.0013 ± 0.0028 | - | Not found | 100 | 0.001± 0.0004 |
| Vardenik river | 80 | 0.0028 ± 0.002 | - | Not found | 100 | 0.005 ± 0.004 |
| Karch Akhpyur river | 80 | 0.008± 0.0006 | 20 | 0.001± - | 100 | 0.0016± 0.001 |
| Arpa river | 50 | 0.0005± 0.00004 | 50 | 0.0001± 0.00005 | 100 | 0.0006± 0.0002 |

DDT was also found in silt (bottom sediments) at the level of 0.01-0.037 mg/kg and HCH was detected at 0.57-1.46 mg/kg. In the muscle tissue of syg-fish (white-fish) DDT was detected at 0.2 mg/kg, DDE was found at 0.1 mg/kg and HCH at 0.2 mg/kg. In 1980-1983, analyses were performed on the muscle tissue of khromulya fish, which is fattier, as compared to white-fish. DDT was found at the level of 0.006 mg/kg, DDE – 0.027 mg/kg and HCH at 0.001 mg/kg.

The results of the studies demonstrated that banning the use of DDT since 1970 and HCH since 1980 (Sevan Lake basin) failed to result in degradation of previously used DDT and HCH in water, silt, and fish from Sevan lake.

However a number of positive changes were observed:

- Decrease of determination percent of these pesticides in samples of water,
- DDT was found at less amounts or was not found, as compared to DDE, thus signifying to degradation of DDT;
- It must be mentioned that DDD was not revealed most likely due to low persistence of this compound.

In 1990s, further studies of Sevan Lake waters demonstrated that DDT and HCH slowly degrade and their levels, as compared to the results of previous studies, were by 1-2 orders less. DDT was revealed at 0.000001 mg/l and HCH made up to 0.000009 mg/l. Deviations from the observed relationship were found, most probably, as a consequence of freshly applied DDT and HCH. It was noteworthy that the decrease of DDT and HCH content in waters of Sevan Lake did not result in significant decrease of these pesticides in muscle tissue of syg-fish (white-fish); this latter was the after-effect of bioaccumulation of these compounds in the organism of fish.

Monitoring studies were performed in 2002 -2003 in order to reveal the current situation.

This time, unlike previous studies, taking into consideration the probable significance of environmental pollution/ contamination due to industrial activity, we performed the first study for the content of polychlorinated biphenyls (PCBs) in open water basins of the Republic of Armenia.

The following categories of open water basins were selected for the study:

1. Water basins, at which there are hydroelectric power plants (rivers Hrazdan, Vorotan);
2. Water basins, at which there are industrial enterprises (rivers Debet and Voghchi);
3. Water basins, at which there are no industrial enterprises or hydroelectric power plants (the Lake Sevan and Arpa river).

Samples of water were taken for analyses by means of gas-liquid chromatography.

The results are presented in Table 3.

Table 3. Average content of Persistent Organic Pollutants in open water basins of the Republic of Armenia, 2002-2003 (in mcg/l)

| | Heptachlor | HCH | | | DDT and metabolites | | | Hexachlorbenzene (HCB) | PCBs |
|---------------------------|-------------|-----------|------------|-----------|---------------------|-----------|-----------|------------------------|------|
| | | α | β | γ | DDT | DDE | DDD | | |
| Sevan Lake | Not studied | Not found | Not found | 0.067 | Not found | 0.016 | Not found | Not studied | 0.61 |
| Rivers flowing into Sevan | Not studied | Not found | Not found | 0.06 | Not found | 0.014 | Not found | Not studied | 0.50 |
| Arpa river | 0.074 | 0.19 | | 0.074 | 0.53 | 0.25 | 0.83 | 0.02 | 1.57 |
| Vorotan river | Not studied | 0.18 | Not found. | 0.20 | 0.13 | 0.16 | 1.68 | 0.036 | 1.49 |
| Vokhchi river | Not studied | 0.04 | 0.02 | 0.04 | 0.02 | 0.01 | 0.007 | Not studied | 1.33 |
| Araks river | Not studied | 0.07 | 0.01 | 0.005 | Not found | Not found | 0.05 | Not studied | 1.74 |
| Pambak river | Not found | Not found | Not found | Not found | 0.02 | Not found | 0.01 | 0.006 | 0.83 |
| Debet river | Not studied | 0.13 | | 0.01 | 0.004 | 0.004 | Not found | Not found | 0.68 |
| Hrazdan River | Not studied | 0.035 | 0.015 | 0.06 | 0.09 | 0.007 | 0.06 | Not studied | 1.82 |

The content of POPs in bottom sediments was also studied (table 4)

Table 4. Average content of Persistent Organic Pollutants in bottom sediments of some water basins of the Republic of Armenia, 2002-2003r (in mcg/l)

| Water reservoirs | Heptachlor | HCH | Lindane | DDT | DDE | DDD | HCB | PCB |
|------------------|------------|---------------------------------------|---------|------|-----------|-----------|-----------|--------|
| Vokhchi river | - | 10.55/ α / 0.34 / β / | 1.63 | 0.66 | 2.90 | Not found | - | 98.37 |
| Pambak river | Not found | 0.11 | 0.19 | 0.79 | 0.41 | 0.15 | Not found | 68.03 |
| Debet river | - | 0.39 | 0.17 | 0.20 | Not found | 0.13 | Not found | 719.06 |

Determination of PCBs in samples taken from open water reservoirs of the 3rd category demonstrated that PCBs were detected in the range from 0.07 to 0.93mcg/l. PCBs average concentration in water samples from the a.m. reservoirs was 0.61-0.83mcg/l.

In samples of water taken from rivers belonging to the 1st category the content of PCBs was 2-fold higher than in water samples from reservoirs of the 3rd category. In these samples PCB residues ranged from 0.44 mcg/l to 2.93 mcg/l. Average PCB concentration in such reservoirs was 1.49 – 1.82 mcg/l.

Study of water samples taken from the rivers, in the water collection area of which there are enterprises having potential to contaminate the environment by PCBs (2nd category), revealed that from the point of view of PCB-induced contamination these samples were in an intermediate state. Residues of PCBs made from 0.44 to 1.68 mcg/l. Average PCB content in these samples was 0.68-1.33 mcg/l.

The results obtained through studies at rivers Arpa, Vorotan, Voghchi, Debet for DDT and α , β - HCH signify to the fresh application of these pesticides in agricultural practice of Armenia, as due to the persistence thereof, these compounds should have degraded long ago.

Unlike our previous studies, such POPs as Hexachlorbenzene, Heptachlor, total PCBs were found in open water basins, but their presence in water reservoirs is connected with a number of technical and technological processes in such branches of industry of the Republic of Armenia as energy production, mining and extracting, metallurgy, etc.

Our findings revealed that the environment of Armenia is entirely contaminated, especially by PCBs, thus indicating to the presence of PCBs in soils, whereof they mainly penetrate to the open water reservoirs. Power engineering system is the main source of PCBs-related contamination in Armenia.