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Chlororganic compounds in the aquatic environment - origin and effects

1. Sources of chlororganic compounds

With a few exceptions, chlororganic compounds occur in our environment because of anthropogenic activities. Among these activities are industrial productions, chemical cleaning of clothes, degreasing of metals and the use of chlorine containing cleansers at various working places and in households.

Among other important sources of chlororganics, we have to consider the use of chlorine for disinfection in drinking water treatment facilities and even in waste water treatment plants leading to the formation of huge amounts of chlororganics released into the environment. In western countries, the use of chlorine as main agent for water disinfection has been faced out since decades. This fact should stimulate public awareness and discussion of arguments.

2. Ways of distribution

Depending on the type of use and the chemical composition, chlororganics are released into the environment through evaporation during or after use, through the canalisation or through the soil into the groundwater. If they are not degraded through photochemical reactions or biochemically, they will finally reach the rivers and the sea. As in Ukraine, river water is the main source of drinking water, chlororganics can be included into this distribution pathway even several times. These considerations underline the need to control the use and the distribution of chlororganics and to include them into an effective monitoring program all over Ukraine. A second reason to demand the monitoring of chlororganics is Ukraine's intention to approach the EU. This requires implementing the Water Framework Directive (WFD) [1] and the types of monitoring programs that are specified in the WFD. Various types of biological and hydromorphological investigations and chemical investigations, including chlororganic compounds, have additionally to be taken into account for the determination of the "ecological status" and the "chemical status" of surface waters.

3. Methods

So far, the monitoring and controls of chlororganics by state or municipal laboratories are limited to gaschromatographical analyses that mainly can identify more or less volatile compounds. This sometimes leads to the impression that chlororganics are not a problem. Non-volatile chlororganic compounds however can only be detected with other methods. The usual and efficient method in many western countries for the control of waste water and surface waters is the AOX, EOX or TOX method. AOX means adsorbable organic halogens, EOX extractable and TOX total organic halogens. In Ukraine, these methods have not yet been certified and can not be used for official monitoring. Correspondingly, equipment is also lacking and funds for purchasing such equipment

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could often be too low.

This article is based on investigations of adsorbable organic halogens (AOX). The method comprises the sum of organic bound chlorine compounds. The singular steps of the method are given in the following table. For more details, see [2].

Table 1. Steps of AOX analysis

	main steps of AOX analyses	determination of organic load
1	sampling (avoiding volatile compounds to escape)	taking parallel sample(s) for further measurements
2	sample stabilisation (+ HNO_3 to pH 2) in the field	cooling during transport
3	dilution (if TOC > 10 mg/L), addition of KNO_3 and activated carbon (pH 2-3)	storage at 4 ^oC (usually < 24 h) in the laboratory
4	storage over night (in case of surface water) at 4 ^oC	analysis of TOC (if not possible, another parameter correlated with TOC)
5	shaking for about 2 hours	
6	filtration through Cl-free membrane filter	
7	washing out inorg. Cl with KNO_3 solution	
8	burning the activated carbon + membrane filter at 960 ^oC in an oxygen stream	
9	coulometric titration of chloride	

To study possible toxic effects of drinking water, toxicological tests have been carried out with Ceriodaphnia affinis *Lilljeborg* as test organism (in accordance with the Ukrainian norm КНД 211.1.4.056-97 [3]. Drinking water samples have been treated physically (boiling, stirring to strip out the volatile compounds) and chemically (using different types of absorbents and flocculation with $FeCl_3$) to reduce the concentration of toxicants, study their behaviour and thus focus on the type of chemical compound. Details are given in [4]

4. Occurrence of chlororganics in the environment and their evaluation

Chlororganic compounds are widespread in tap water, they occur in groundwater and rivers (see table 2, fig. 1 and 2). In tap water, they originate from disinfection of raw water (before the cleaning process) and the disinfection of clean drinking water [5]. Only a few singular compounds as for example chloroform are regularly analysed in the water works laboratory. This is necessary, to control if the water is within the limits for drinking water.
In the EU too, a threshold value for AOX has not been defined, only a guide values exist (5 μg/L). This value has also be set as target value for cleaned drinking water by the city of Amsterdam (NL). There as well, polluted river water (from the Rhine River) is abstracted for further treatment. Chlorine is not used, the raw water is however infiltrated into the underground for a first cleaning and then pumped back for further treatments.

The occurrence of chlororganics in river water is widespread in industrialised countries. The AOX concentrations found in Ukraine during the last seven years are however high compared for example to the findings in Germany. Official German publications [6] have classified AOX-values > 50 μg/L as clearly loaded. More than 100 μg/L indicate a “high load” with chlororganic

Tab. 2: Results of AOX monitoring (mean and singular values in microgram per liter)

time of sampling	location	number of samples	AOX µg/L
Dec. 1993	Kiev	28	329
July 1996	Zaphoroshije	5	327
June 1997	Odessa	2	266
June 1997	Slavutitch (from groundwater)	2	44
July 1997	Kiev	11	311
Aug. 1997	Sewastopol	1	521
Sep. 1997	Lvov	3	170
Oct. 1997	Kirovograd	1	431
Nov. 1997	Kiev	2	157
Nov. 1997	Charkov	1	268
Dec. 1997	Lugansk	1	362
(winter) 1997/98	Kiev	10	140
(summer) 1998	Kiev	20	260
Feb. 1999	Kiev	7	80
May 1999	Kiev	2	159 / 202
June 1999	Kiev, only centre	5	100 - 140
Sept. 1999	Kiev	7	32-132
May 2000	Kiev, right bank side (Dnepr-water work + groundwater)	1	115
June 2000	Kiev, left bank s.. (Desna- ww.)	1	300
July 2000	Kiev, right bank side	2	113 / 137
Dec. 2000	Kiev, right bank side	3	260 / 330 / 440
Mar. 98 - May 2000	raw water from river Desna	7	min-max: 15 - 167
Nov.97-Dec. 2000	Dnepr (Kiev + K. reservoir)	11	min-max: 22 - 160

compounds. AOX concentrations, found in Kievs' main drinking water resources, the Dnepr and the Desna river, are between 20 and 170 µg/L

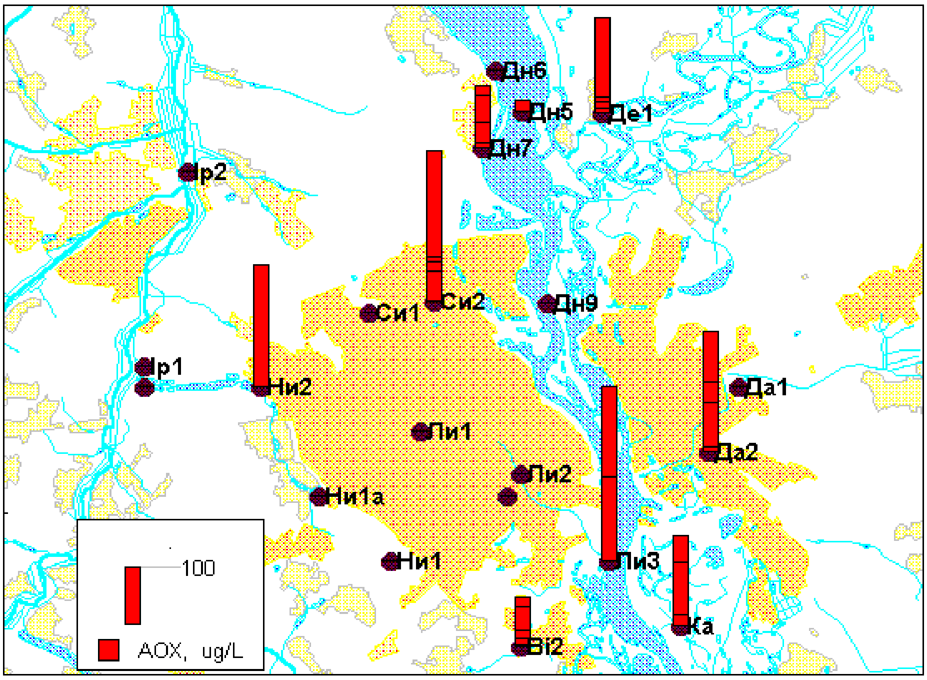

Fig. 1: results of AOX measurements (maxima) in Kiev between 1998 and 2000 (black marks within the columns show some singular results)

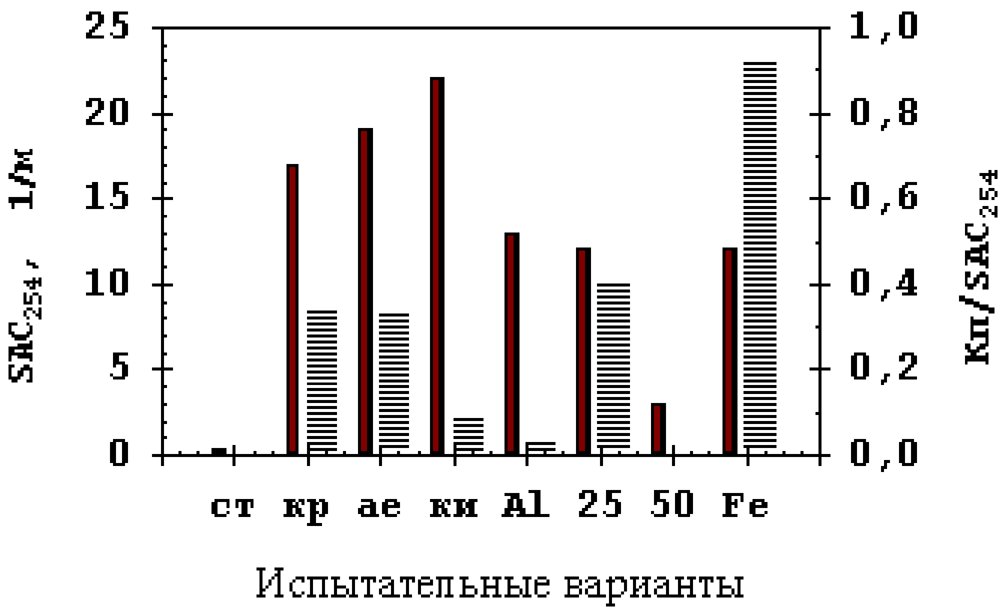

Fig. 2: Comparison of the organic load (SAC 254) of the test variants (thin columns) and the quotient dead organisms related to the concentration of organics (Кп/SAC 254), striped columns; abbreviations: ст = standard, кр = unchanged tap water, ае = tap water after 1 hour of intensive aeration, ки = tap water after 5 minutes of strong boiling, AL = treated with Al2O3, 25 = treated with 0,25 g/L activated carbon, 50 = treated with 0,5 g/L activated carbon, Fe = treated with 0,5 g/L FeCl3

5. Consequences

As has been described in [7], chlororganic compounds that have been found in streams of bigger cities can be significantly toxic or mutagenic. Concentrations above 50 μg/L are likely to produce those effects. Further consequences are not yet fully overseen.

In drinking water, a huge quantity of different chlororganic compounds can occur. They are all not suitable and differ with regard to their behaviour in living organisms and their toxic effects. About their combined effect even less is known. Among the better known toxic compounds is chloroform that should not occur in higher concentrations than 80 μg/L in Ukraine. High concentrations in tap water are observed during times of strong phytoplankton development. Other toxic compounds found in drinking water are chlorinated acetic acid that can be used as an insecticide. In the EC directive 76/464/EWG a guide value of 10 μg/L in rivers has been defined for this compound. Another problematic group of compounds are chloramines. Higher chloramine concentrations are formed through the addition of ammoniac (NH3) in the water work aiming at reducing chlorine consumption and chloroform formation. Concentrations up to several mg/L are reported as not dangerous for humans, but the aquatic fauna is highly sensitive and concentrations as low as 70 μg/L can already be detrimental. This must be taken into account if the sewage treatment plant does not sufficiently eliminate those compounds and discharges them into a river with insufficient dilution.

If tap water is pre-treated as mentioned in chapter 2, toxicity is not completely removed. Figure 2 shows the effect of the different pre-treatment types. The comparison leads to the conclusion that the used test organism C. affinis L. seems to be very sensitive against compounds that have a rather small molecular size. Further, one must take into account that living aquatic organisms have adsorptive body surfaces that can adsorb reactive elements and hydrophobic non-polar substances [4]. Chlorinated acetic acid could be one of those compounds that are dangerous for humans or the environment.
How far this so far unknown compound can also be detrimental for humans can, of course, not be proven by such tests. Much more informative are statistical medical investigations as have mainly been carried out in the US. They have shown increased risks of colon cancer and total combined cancer as for example in the Iowa Women's Health Study that was published in 1997 [8].

6. Recommendations

Chlorine is a by-product of the chlorine-alkali electrolyses. The use of chlorine and other by-products as vinyl-chloride (VC) and its derivatives has more and more been decreased in western countries. PVC for example can be and is replaced by other less dangerous materials (example: toys, window frames). Chlorinated cleaning solutions can be replaced and effectively cleaned waste water is not disinfected at all. For the disinfection of drinking water, other methods are available, but sometimes they are also not free of problems. If there is no alternative, chlorine dioxide is used for disinfection, leading to lower concentrations of chlororganics that can be further eliminated through activated carbon filtration.
More recommendations and practical hints should be made known to the public. This can lead to a decrease of chlororganics in our environment as it was the case in Germany during the years 1985 - 1995 (fig.3). An important tool to reach this goal, are effective controls of wastewater

discharges (emissions) and surface waters (imissions). The AOX method is recommended here for a cost-effective and quick alternative to GC screenings.

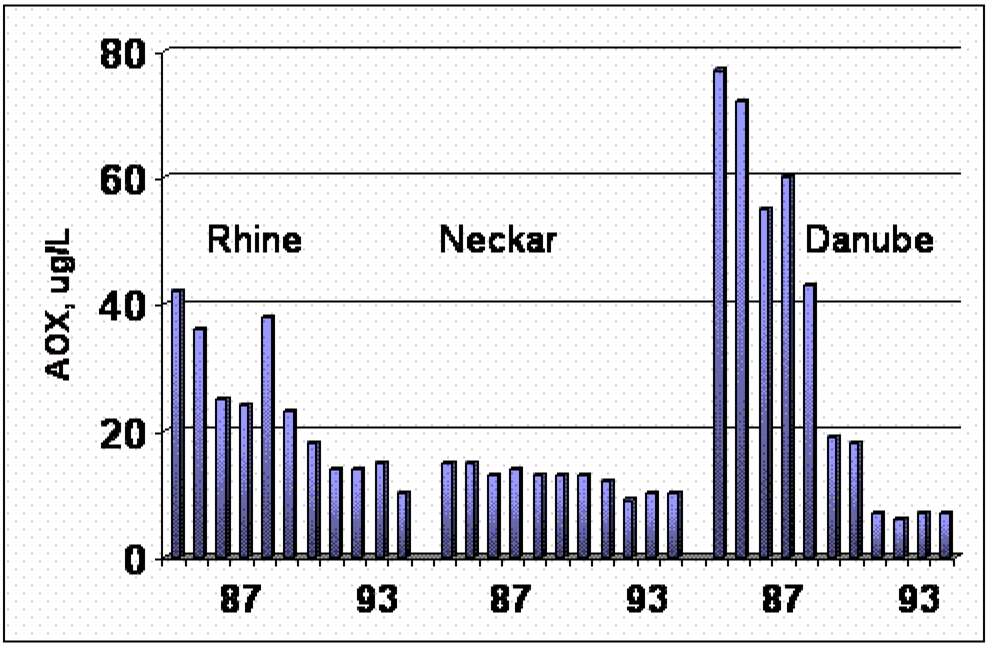

Fig. 3: Decrease of AOX values between 1985 and 1995 in German rivers

7. Summary

Chlororganic compounds are by far more widespread in Ukraine as one supposes because their occurrence is only poorly controlled. This is due to analytical restrictions and design of monitoring programs. For the here described investigations, the AOX method has been used as a screening method for measuring the sum of adsorbable organic halogens (AOX).
The analytical results indicate that tap water in the bigger Ukrainian cities is usually enriched with chlororganics up to 500 µg/L or sometimes-even more. This is about 100 times more than European guideline values. Only a few chlororganics as chloroform are regularily controlled, the by far biggest part of substances cannot be identified with usual routine methods and remains unknown. Hints on disadvantages for human health have been gained from statistical investigations in the US. They have proven that chlorination by-products in drinking water increase the risk of cancer and other types of illness.

Chlororganics in river water are even less monitored but random samplings have shown that this is urgently necessary. It has to be assumed that the occurring types of chlororganics differ from those found in urban tap water and that the detected concentrations can have negative biological effects (Yamamoto et al. 1992).

Резюме

Хлорорганические соединения более широко распространены в Украине чем предполагается, поскольку их распространение недостаточно контролируется. Это происходит из-за аналитических ограничений и разработки мониторинговых программ. Для описанных исследований был использован метод AOX для измерения суммы адсорбированных органических галогенов (AOX).

Результаты показали, что водопроводная вода в больших городах Украины наполнена хлорорганическими соединениями до 500 μг/Л (микрограмм/л), а иногда даже и больше. Это в 100 раз больше чем Европейские директивы. Уровень только некоторых хлорорганических соединений, таких как хлороформ, регулярно контролируется, поскольку большинство веществ невозможно определить при помощи обыкновенных методов и они остаются неизвестными. Согласно проведенным в США исследованиям, эти вещества оказывают негативное влияние на здоровье людей. Было доказано, что хлорирование субпродуктов в питьевой воде повышает риск заболевания раком и другими болезнями.

Исследования хлорорганических соединений в речной воде проводятся еще реже, а образцы показывают, что это крайне необходимо. Типы хлорорганических соединений в речной воде отличаются от тех, которые есть в водопроводной воде и они могут иметь негативные экологический эффект (Yamamoto et al. 1992).

8. Literature

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