# SECONDARY DIOXIN POLLUTION OF WATER IN THE PROCESS OF CHLORINATION

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## Introduction

Dioxins may get into water with precipitation, dust and waste waters. Biological waste water treatment is traditional for Russia and it often includes chlorination as the final stage of purification. Biological waste water treatment facilities in the city of Sterlitamak collect industrial and municipal waste waters. Industrial waste water passes through the primary settling reservoirs and then it is mixed with municipal waste water in a mixer. The mixed waste water further on goes to aerotanks, then after secondary settling reservoirs it is processed with sodium hypochlorite in proportion of 1.5-2.5 mg of active chlorine per liter. The total time of water treatment in biological treatment facilities is 20-24 hours. Waste incinerators and production of chlororganic compounds in the city of Sterlitamak are sources of water pollution by PCDD/PCDF. The aim of this research is to determine the possibility of PCDD/PCDF formation at the stage of waste water chlorination after its biological purification.

## Materials and Methods

For the analysis the samples of waste water before and after chloronation at a biological water treatment plant were collected. The samples were taken in specially prepared vessel in volume 10 litres. Sampling and sample preparation for analysis were performed in compliance with recommendations of US EPA 1613, as reported[1)]. For control of sample preparation process isotope-labelled standards $^{37}$Cl-2,3,7,8-TCDD, $^{13}C_{12}$-2,3,7,8-TCDF, $^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF and $^{13}C_{12}$-OCDD were introduced into all samples. Water samples were extracted with three portions of hexane. The water filter was extracted in a Soxhlet extractor with toluene. Toluene was substituted by hexane. The extracts were cleaned by silica gel and charcoal columns. The analysis was performed using a mass-spectrometer Incos 50 equipped with a chromatograph Varian 3400 and a capillary column DB-5MS in the selected ion-monitoring mode. The internal $^{13}$C-labelled standards $^{13}C_{12}$-1,2,3,4-TCDD and $^{13}C_{12}$-1,2,3,6,7,8-HxCDD were used for calculation of mass-chromatograms. Analysis error was 60%.

## Results and Discussion

The results of the analyses are as follows: the PCDD/PCDF contents in the purified waste water is up to 0,021 ng/l-TEQ (both before and after chlorination), in active sludge 0,003-0,06 ng/g-TEQ. The main congeners of pollution are hepta-, octachlordibenzofurans and octachlordibenzodioxins.

Thus, it is possible to tell, that the level of water pollution is insignificant. However there are some samples with overestimated TEQ-contents, mainly, at the expense of 2,3,7,8-TCDF appearance. Thus the sample of water with PCDD/PCDF contents 0,021 ng/l-TEQ had 0,19 ng/l 2,3,7,8-TCDF. There were two samples taken before chlorination with extremely high contents of 2,3,7,8-TCDF - 3,30 and 1,24 ng/l, which first were mistaken for errors. To find out the cause of high 2,3,7,8-TCDF concentration in samples of purified waste water, we carried out chlorination of the purified waste water by sodium hypochlorite under laboratory conditions. At different times three samples of the purified wastewater before chlorination were collected. In to sample water of volume 5 liters sodium hypochlorite was added with active chlorine excess by 100 times – 150-250 mg of active chlorine per liter. The sample had been mixed for 48 hours at room temperature and analyzed as is specified above simultaneously with the control sample of purified water. In the control samples of water the contents 2,3,7,8-TCDF was determined as "not detected" at the detection limit 0,01 ng/l. In treated samples of water the contents of 2,3,7,8-TCDF were found 2,09, 0,54 and 0,88 ng/l. Mass-chromatograms of the treated and untreated water are given in Fig. 1,2. Addition of phenol . in to waste water does not result in the increase of the 2,3,7,8-TCDF contents. A possible mechanisms of 2,3,7,8-TCDF formation is chlorination of dibenzofurans present in water. It can also be assumed that under plant's condition 2,3,7,8-TCDF formation happens at the unauthorized discharge of sodium hypochlorite in to waste water during the process of production of technical sodium hypochlorite.

**Acknowledgements**

At normal operational mode of chlorination unit of wastewater after biological treatment the formation PCDD/PCDF does not happen.
In extreme cases of increase of a doze of active chlorine the formation PCDD/PCDF is possible**.**

**References**

1. Khizbullin F, Muslymova I, Khasanova I, Chernova L and Abdraschitov Ja; *Organohalogen Compounds*. **1998**, 36, 225.

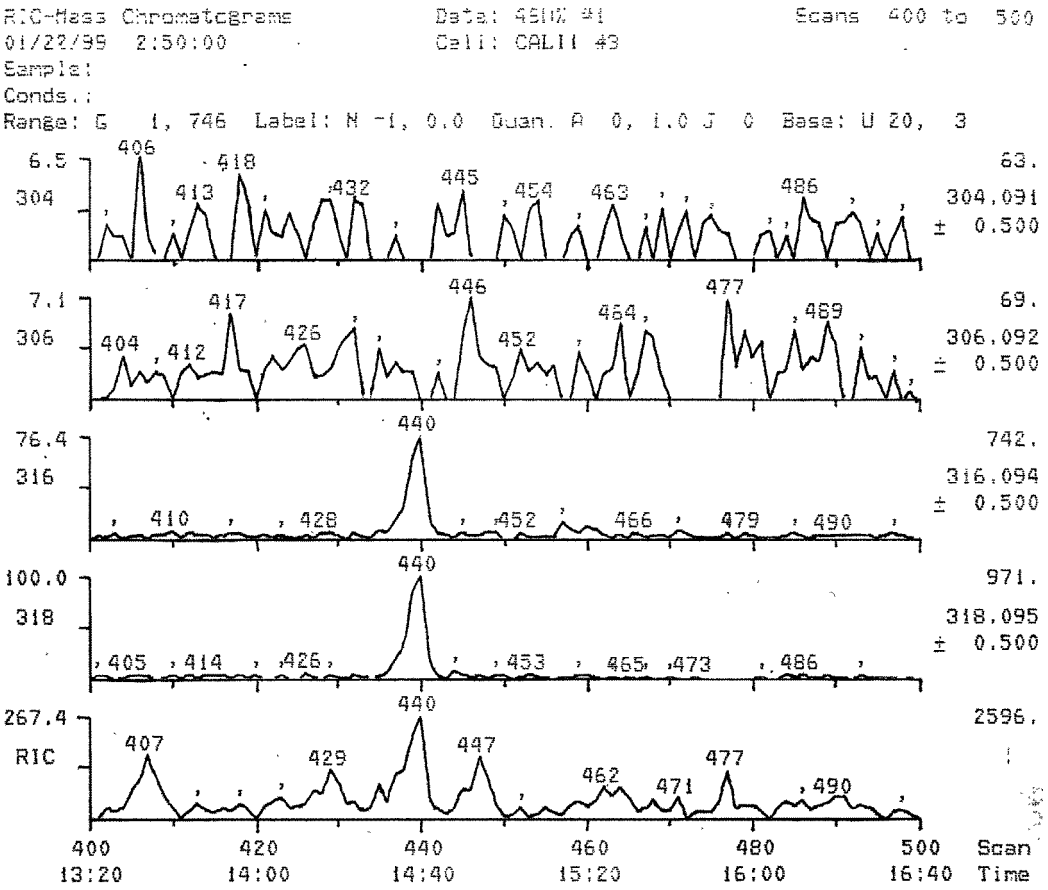


Fig. 1 Mass-chromatograms of untreated water with standard $^{13}C_{12}$-2,3,7,8-TCDF.

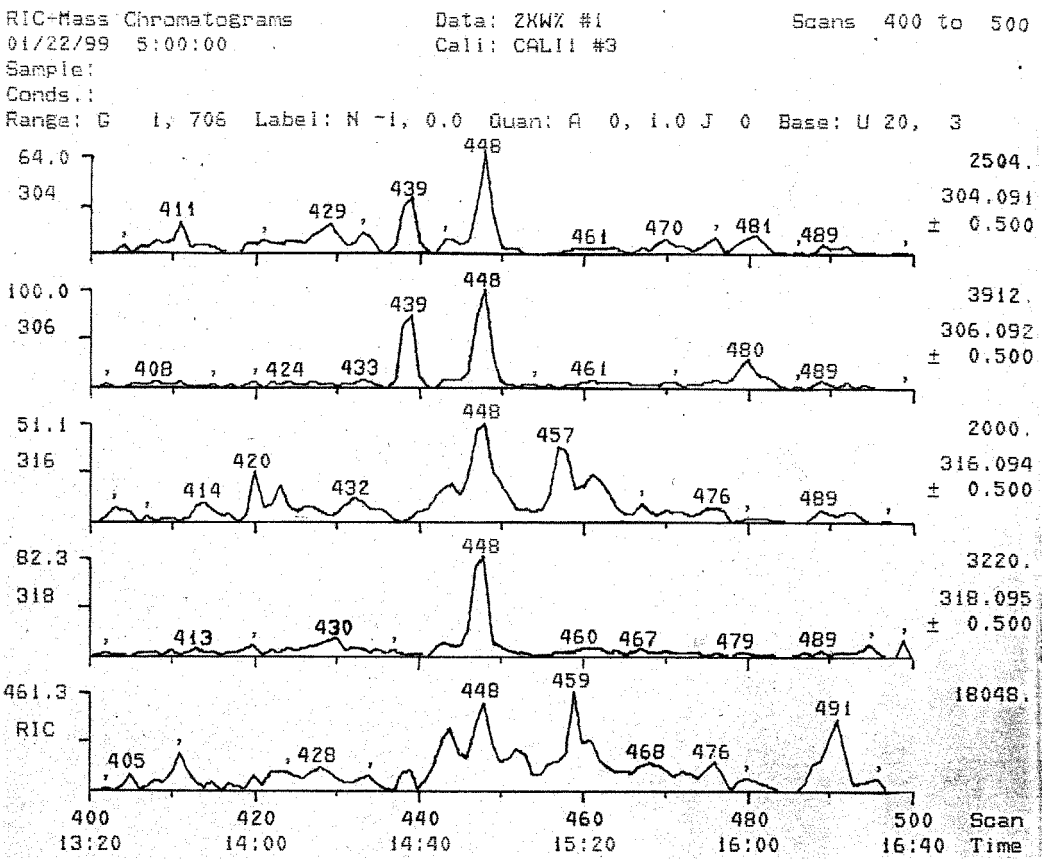


Fig. 2 Mass-chromatograms of water treated by hypochlorite with standard $^{13}C_{12}$-2,3,7,8-TCDF.