

## A Possible Source of Dioxin Contamination of Ambient Air in the Vicinity of Pulp and Paper Mills

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### Abstract

A very high PCDDs/PCDFs concentration in ambient air in Novodvinsk town nearby Arkhangelsk is shown to be caused in a great part by aerosol formation due to intensive air bubbling through slime heaps in pulp and paper mill and flue gas of chemical recovery boilers.

### Introduction

It was shown in the report of the expedition along Arkhangelsk region in 1993<sup>1)</sup> that ambient air in the Novodvinsk town, a small town nearby Arkhangelsk, where a big pulp and paper mill (PPM) is situated, is hard polluted by dioxins. The air sample collected in the center of the town was found to contain PCDDs/PCDFs over 2000 pg/m<sup>3</sup> total or 44 pg/m<sup>3</sup> in I-TEQ (limit allowed level in Russia is 0.5 pg/m<sup>3</sup>). Isomer profile of the dioxins in this sample (Fig.1) is different from that of flue gases of chemical recovery boilers (CRB) burned by pulp and paper mill wastes containing chlorine bleaching residues.

Moreover dioxin concentration in CRB flue gases (250000 m<sup>3</sup>/h; 30-70 pg/m<sup>3</sup> total, 1-5 pg/m<sup>3</sup> in I-TEQ) was not enough to lead to such high level dioxin concentration in ambient air. Therefore it was evident that there is other powerful source of dioxin emission into atmosphere. It is known that sometimes a comparison of PCDD/PCDF congener profile in samples from various dioxin sources can make clear a possible contamination source<sup>2,3)</sup>. Therefore this source can be probably a combustion furnace in the power plant (combusting coal as fuel), slime scattering from slime fields, transboundary transport or somewhat else.

### Results and discussion

To establish a dioxin source responsible for high PCDD/PCDF concentration in ambient air in Novodvinsk the congener profile of PCDD/PCDF in the air sample was compared with that of in various samples collected in sites possibly related to typical dioxin emission sources: slime heaps, dumps, slimes, soil near power plant burned by coal, etc. collected in Novodvinsk, Arkhangelsk and Arkhangelsk region. These data were treated using factor analysis method. The correlation matrix of PCDD/PCDF concentration in 29 samples of air (A\_N), CRB flue gases (A\_1 - A\_3), slime heaps (A\_4\_5, A\_C\_1, A\_C\_2, A\_Syk\_3), soil from dumps (A\_4\_1 - A\_4\_4), other soil and sediment (A\_1\_16 - A\_1\_20) was used. The correlation matrix was treated by principal component method and varimax factor rotation was used to maximize difference between objects. Three significant factors were obtained with eigenvalues

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taking 66, 15 and 8% of the total variance, respectively. Factor loadings for these factors are shown in the Fig.2. The major loading on the first factor is OCDD, on the second - OCDF, on the third - 2,3,7,8-TCDD, 2,3,7,8-TCDF, 1,2,3,4,6,7,8-OCDD and 1234678-OCDF.

In the Fig.3a the factor scores for the first two factors are shown. The sample points are grouped in some clusters. The most of the points form a group in the right part of the figure. Several points including the point of the air sample A\_N, soil sample A\_4\_6 from end face of the chlorine plant in Arkhangelsk PPM, slime sample A\_Syk\_3 and sediment A\_Syk\_2 from Syktyvkar PPM, etc. may be assembled in the group in the left side. Some points, CBR flue gas sample A\_3, and to a lesser extent A\_4\_5, dewaterized slime sample from Archangelsk PPM slime tank, soil sample from damp A\_4\_2, are intermediate.

Basing on the first factor scores the air sample is very different from the most of other samples. Therefore dioxin congener distribution in this sample is differ from that of soil samples in which a contribution of combustion products can be expected. But it must be considered that the first factor scores for slime samples are vary along the all interval of the score values and the value for the air sample is within this interval.

The second factor scores for the slime samples are closely spaced and the value for the air sample is also within this interval closer to the slime sample A\_4\_5 from Arkhangelsk PPM.

The third factor scores are essentially the same for all soil and slime samples except for the A-Syk-3 (the slime sample from Syktyvkar) while those of the air and CBR flue gas samples are differ from them. Therefore it can be considered that CBR flue gases give a contribution in air contamination but this contribution corresponds to the factor with minimal variance.

Consequently slime heaps can be proposed as a possible source of dioxin emission in ambient air. The mechanism of this dioxin emission can be suggested as follows. Biological degradation of wastes is occurred in aeration tanks - open basins 100 m x 10 m through which 300,000 m<sup>3</sup>/hour air is bubbled continuously. Powerful mixing produces thick foam, going by the wind. It was shown elsewhere<sup>1)</sup> that dioxin content in slime is rather large: 2063 pg/kg (in I-TEQ), thus large amounts of dioxins can be emitted with aerosol particles.

Therefore, slime heaps with air bubbling can be considered as a source of dioxin contaminated aerosol formation which can transport dioxins on a long distance. This chlorine containing aerosol is a result of chlorine bleaching. This novel dioxin contamination source should be payed into attention when dioxin emission, transport and balance are considered.

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## Literature Cited

- (1) Assessment of dioxin contamination and revealing dioxin emission sources in Archangelk and the Archangelk region, Report of international expedition, Moscow, 1993-1994, 174 p.
- (2) V.Zitko. The Science of the Total Environment, 1989, **80**, 127-137.
- (3) Smith R.M.; P.W.O'Keefe; K.M.Aldous; H.Valente; S.P.Connor; R.J.Donnely, Environ.Sci.Technol. 1990, **24**, 1502-1506.



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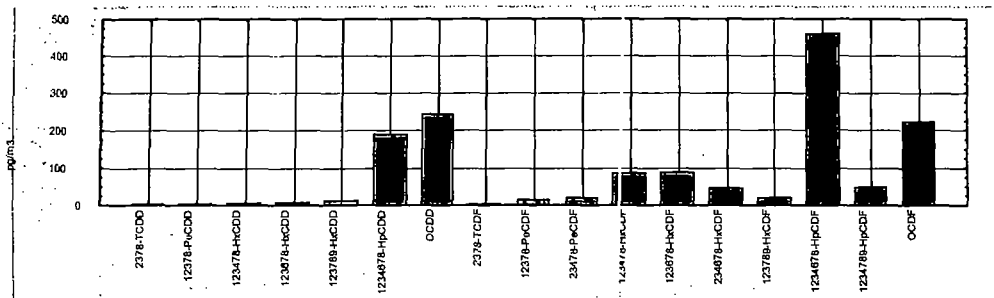


Fig.1. PCDD/PCDF congener distribution in air sample from Novodvinsk

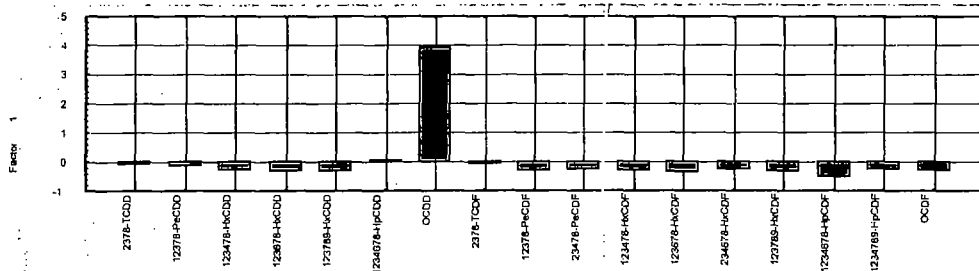


Fig.2-a. Factor 1 loadings

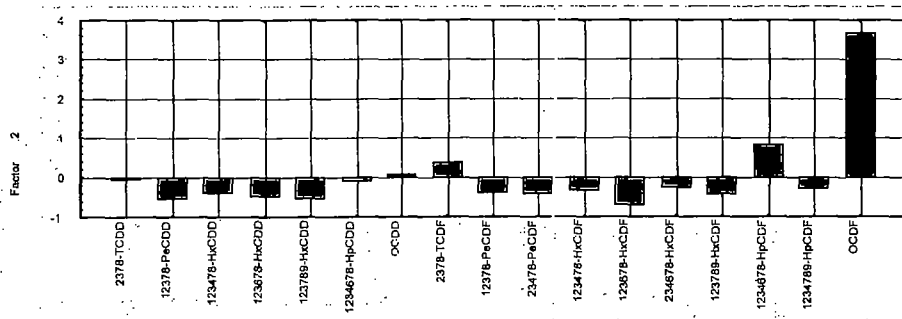


Fig.2b. Factor 2 loadings

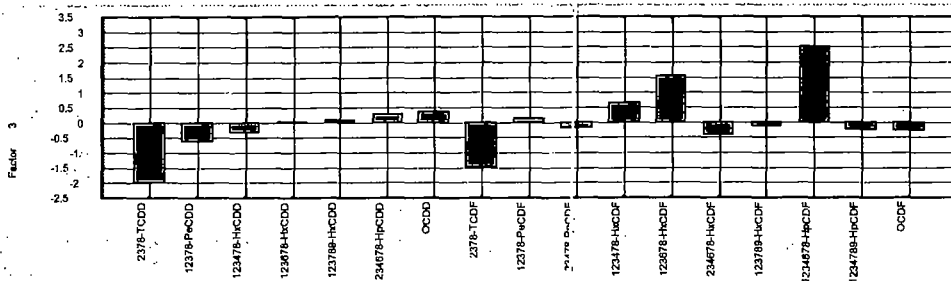


Fig.2c. Factor 3 loadings