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Deposition of volatile organic compounds into surface water at the case study of aldehydes at Oltchim SA

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Abstract- Together with the industrial development the awareness of the Romanian society towards environmental protection has increased steadily. "Visible" pollution like smoking exhaust gases from chemical plants, smell in the air or litter pollution of surface water has raised most of the public concerns so far. Compared to other pollutants like Sulfur, Heavy Metals, Dust or Oil the mass amount of volatile organic compounds is very small. But most of these substances are easily water soluble and very reactive. Due to this reactivity even small amounts of organic compounds can have a significant effect on water and air pollution. Oltchim SA operates a significant Oxo-alcohol production site in Rm. Valcea, emitting a considerable amount of aldehydes. The deposit of these aldehydes into a sewage drain allows a direct relation between emissions of aldehydes and the relevant imissions in the surface water.

Keywords: VOC, Aldehyde, Oltchim

1. INTRODUCTION

After a decade of strong economic growth also the environmental pollution resulting from industry and traffic has significantly increased in Romania. As emissions mainly greenhouse gases like CO2, NOX and Methane are measured. The quantity of none of these substances could be reduced during the last decades (see Fig. 1-3). Only the content of organic compounds (hydrocarbons) could be reduced due to new filter technologies and the usage of new catalysts, in traffic and in industry (Fig. 4).

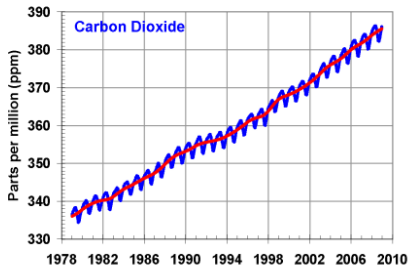

Fig. 1 Evaluation of CO2-content in atmosphere

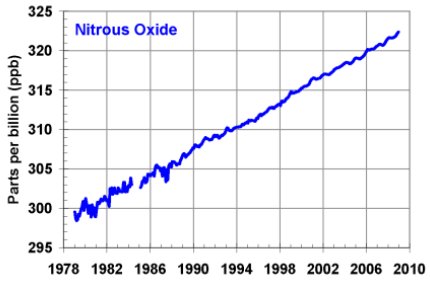

Fig. 2 Evaluation of NOX-content in atmosphere

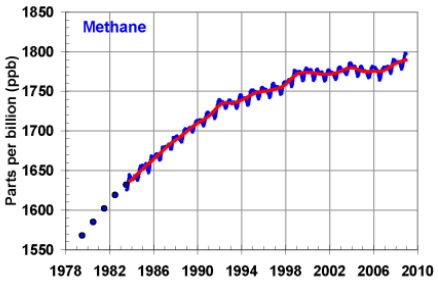

Fig. 3 Evaluation of methane-content in atmosphere

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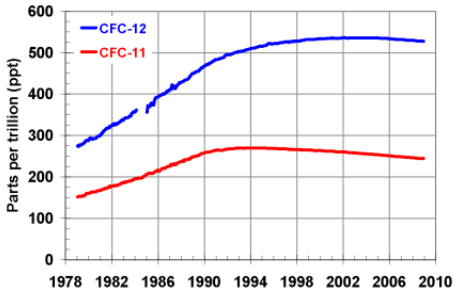

Fig. 4 Evaluation of Hydrocarbon-content in atmosphere

2. VOLATILE ORGANIC COMPOUNDS, VOC

Compared to traditional monitored emissions like sulphur or dust, the emissions of VOC have only a small mass. Nevertheless these substances are very reactive and already a small amount can have a significant polluting effect when deposited in surface water. As sampling and analysis of these substances in water and air are difficult there exist only few case studies proving that VOC are deposited also in surface water.

In the last years several countries within the EU have defined allowed max. limits in air for a group of VOC like aldehydes, amines and cyclical hydrocarbons, as the cancer causing potential of these substances has been detected. The effects of VOC in water, and if their carcinogenic potential also remains in water is under evaluation within the last years.

Oltchim SA operates a significant oxo-alcohol production site in Rm. Valcea. The production capacity is 52.000 tons/a. Due to the process there are significant emissions of aldehydes, amounting to 1.600 – 2.000 tons/a. Close to the oxo-alcohol production is passing by a sewage water canal with a flow of approx. 1 m^3/s (see fig. 5).

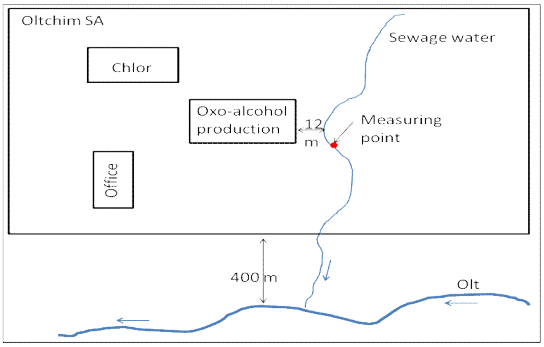

Fig. 5 Oltchim SA

3. ALDEHYDES AS POLLUTANT

Aldehydes have hardly been considered as pollutant so far and the emissions are very small in respect to the share of mass of the total emissions. On the other hand they have a considerable effect on numerous chemical reactions in the atmosphere and surface water.

Aldehydes are formed through oxidation of primary alcohols. An oxidation means the substitution of 2 hydrogen atoms; this reaction has also lead to the name for the aldehydes: („Alcohol dehydrogenatus“). Following common particular characteristics in the molecular structure aldehydes can be divided into different groups:

- saturated unbranched or branched aliphatic aldehydes (IUPAC name: n-and i-alkanals) such as Methanal (older name: formaldehyde), n-hexanal, 3-methylbutanal, 2-ethyl hexanal,
- saturated cyclic aldehydes, for example Cyclohexylmethanal,
- aromatic aldehydes such as, for example Phenylmethanal (benzaldehyde) and unsaturated cyclic aldehydes as 2-Furylmethanal (furfural),
- mono- or polyunsaturated aldehydes (alkenals, Alkadienale) such as propenal (acrolein), trans-Butenal (crotonaldehyde), 3-phenylpropenal (cinnamaldehyde)
- polyvalent aldehydes (Alkandiale) such as ethanedial (glyoxal), propandial (malondialdehyde), Pentandianal (Glutaraldehyd)

Aldehydes are partly emitted from natural sources like plants or forest fires. The main shares are man-made, mainly from combustion processes.

Table 1 Emissions of aldehydes

Combustible	**Firing**	**Emissions (g/GJ)**
Gas	Industry	1,2
Oil	Good combustion	2,6
	Bad combustion	7,1
Coal	Good combustion	0,07
	Bad combustion	0,1

The whole carcinogen potential of aldehydes is not yet fully explored. For some of the aldehydes exist more detailed data, such as Formaldehyde which has the following effects:

Table 2 Health effects of aldehydes

Concentration mg/m^3	**Exposure time**	**Remark**
1.100	30 min	50% of rats died
25	1 min	longer stay for humans impossible
11	10 min	hard to withstand
2,4-4	till 8h	only small irritations to eyes and nose
13-26	10 min	difficulties to breathe

4. SAMPLING IN RM. VALCEA

Close to the Oxo-alcohol production has been selected a measuring point at the sewage water canal of Oltchim (Fig. 5). At this measuring point are taken samples every day for a period of 2 months in June and July 2011 to create a profile of the aldehyde concentration within the sewage water canal. Simultaneously is measured the concentration of aldehydes in air.

For the analysis of the samples of water from the Olt are used Denuders. The selected annular denuders are made of sandblasted glass. The tubes are hold together by attached glass sparkles. The adsorbed Aldehydes are extracted from the Denuders with nitric acid. The analysis itself is done by photometry.

5. RESULTS OF THE ANALYSIS

Results of the analysis show that there exists a contamination of the sewage water canal with aldehydes. The maximum concentrations found are 430 µg/l. But in most of the days there could not be detected any aldehydes in the water. The detection limit is 40 µg/l has not been exceeded at these days (Fig. 6+7).

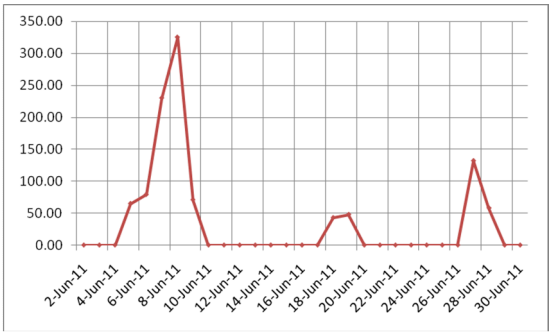

Fig. 6 Aldehydes in sewage water in June 2011 in µg/l

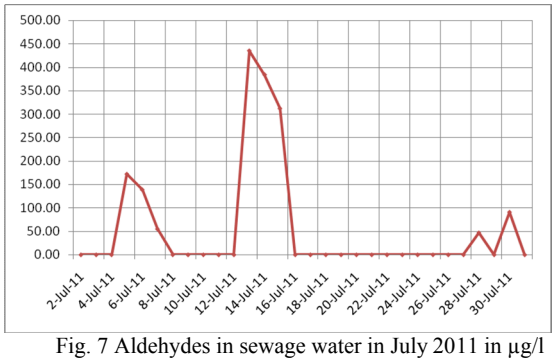

Fig. 7 Aldehydes in sewage water in July 2011 in µg/l

In order to determine why only for a few days aldehydes could be detected further investigations have been made. It shows that aldehydes in air could only be detected if the wind did not blow to strong at the measuring points.

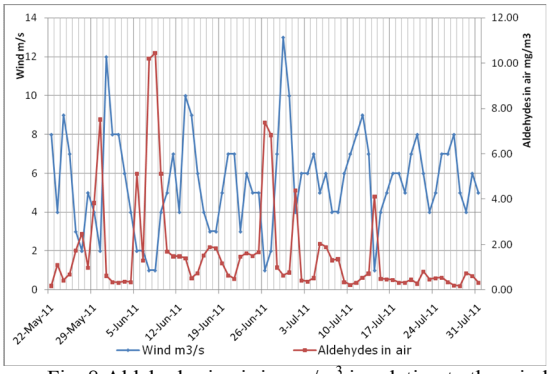

Fig. 8 Aldehydes in air in mg/m^3 in relation to the wind in m/s

Only if the aldehydes in air exceed a certain threshold there could be detected aldehydes within the surface water. It seems that if the concentration in air does not exceed 2 mg/m^3 there cannot be detected aldehydes in water.

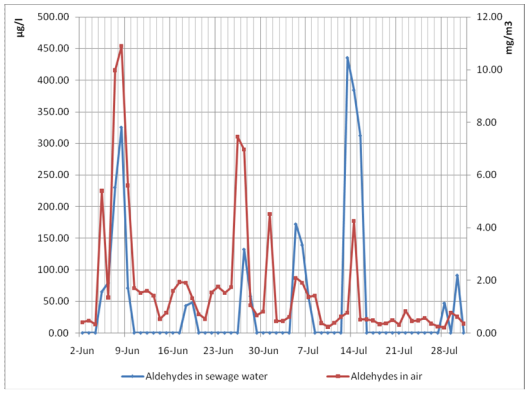

Fig. 9 Aldehydes in surface water in correlation with the aldehydes detected in air.

6. CONCLUSIONS

In Rm. Valcea a considerable amount of the aldehydes emitted are dissolved in surface water. The detection limits are only exceeded if the pollution with aldehydes amounts to more than 40 mg/s.

Pollution / 1 m^3/s = 40 µg/l
Pollution = 40 µg/l x 1 m^3/s = 40 mg/s

At a constant flow rate the total amounts deposited into the sewage water amounts to 1.152 kg/a. This means that a quantity of 0,16% of the total emissions is dissolved only in the sewage water canal.

The results can be used to develop recommendations to reduce the emission of aldehydes in order to minimize negative effects on surface water and nature. It will give a contribution to decide if aldehydes have to be included into the list of substances prioritized by EU-directive 2455/2001/EG.

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