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Economic crisis of Romania, new chance to relate pollution of surface water to contaminator

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Abstract- Due to the economic crisis many industrial companies have reduced or stopped completely their production. By this also pollution of nature and surface water caused by industrial production has been significantly reduced. During economic recovery production plants will restart successively and measured imissions can be selectively allocated to contaminators. This also opens up the chance to better understand physical and chemical reactions and to optimize production processes in order to minimize pollution. The chemical complex Oltchim in Rm. Valcea has stopped main production since Nov. 2008. Oltchim operates the biggest Oxo-alcohol production in Romania and is a significant contaminator of aldehydes. Aldehydes have hardly been considered in the past, even if they can have significant effects on health. Standardized measurements and standardizes methods for samplings don't exist yet in Romania. Denuders have proven to be useful for sampling of imissions and emissions.
Keywords: Aldehyde, Denuder, Oltchim

1. INTRODUCTION

After a decade of strong economic growth companies have reduced industrial production significantly since July 2008 due to the financial crisis. Especially hit by the current crisis are companies with outdated and therefore inefficient production sites. Because of this reason it can be assumed that the emissions into the atmosphere have been reduced more significant than the industrial production.

This is also valid for the biggest chemical complex of Romania, Oltchim in Rm. Valcea, directly located at the river Olt (see Fig. 3). Since November 2008 the main part of the production is shut down. Only when the petrochemical part of the refinery Arpechim in Pitesti restarts operations the necessary raw materials for Oltchim to restart the chemical plants are available. The restart of the petrochemical part of Arpechim is planned for September 2010.

2. OVERVIEW ALDEHYDES

This means nearly two years without noteworthy pollution from the chemical plant for Rm. Valcea, the Olt and its surrounding area. This period is not sufficient to biologically degrade harmful substances or heavy metals that have been accumulated in decades. But for highly volatile and water soluble contaminants it can be considered a complete reduction, especially for contaminants in the Olt itself.

Also, aldehydes are part of this group of pollutants. Aldehydes have hardly been considered 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.

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)

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

Tab. 1 [1]:

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

An important source for aldehydes is the road traffic. Cars with diesel motor achieve better results than those with gasoline motor. In average the share of Formaledhyde is 60% of the total aldehyde emissions, while Acetaldehyde represents 12%. Estimations in the USA amount to 65.000 tons/year total aldehyde emissions from road traffic, 54.000 tons/year from combustion processes and 23.000 tons/year from other industrial processes.

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:

Tab. 2 [8]:

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

3. ACTUAL SITUATION IN RM. VALCEA

Oltchim operates a prominent Oxo-Alcohol production site. In connection with this alcohol production also significant quantities of aldehydes are emitted into the atmosphere.

The actual situation gives the chance to measure the increase of the imissions simultaneous with the putting in function of the chemical production. The time span between emission and entry into the Olt will allow conclusions in regard to the chemical effects happening. The following aldehyds can be measured in water: Formaldehyde, Acetaldehyde, Propionaldehyde, Butyraldehyde, Valeraldehyde, Hexanat and Acrolein.

The total man-made influence on the aldehyde-contamination cannot be established. But with analysis of the headwaters of the Olt and directly after the city the effect of the city of Rm. Valcea can be captured.

With the Directive 2000/60/EC, the EU has created in 2000 a comprehensive scheme for the sustainable use and protection of inland surface water, groundwater and coastal waters to protect the environment and improving the status of aquatic ecosystems. The directive is intended to gradually improve the waters and all member states should reach at least a good water status.

The directive provides that, inter alia:
• Water is a heritage protected, defended and treated as such.
• To avoid a long-term deterioration in the quality and quantity of fresh water extensive measures have to be taken.

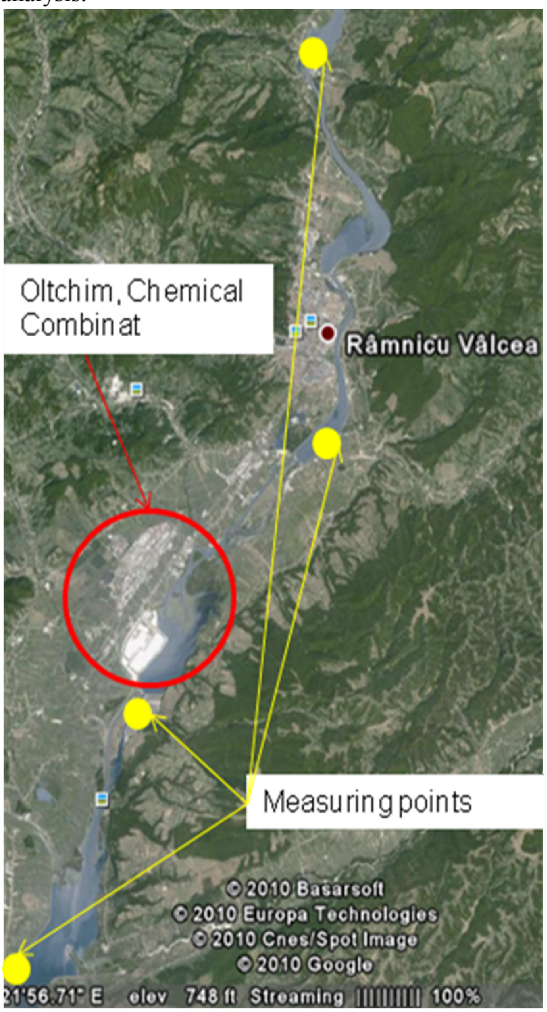
4. SAMPLING IN RM. VALCEA

At the Olt have been selected 4 measuring points within a distance of 20 km (Fig. 1). At this measuring points are taken samples every second day for a period of 2 months to create a profile of the Aldehyde concentration without the chemical complex in operation.

Simultaneous with the restart of the chemical plants the effect on the contaminations of the Olt will be measured. Therefore in September, when planned restart is carried out, similar measures will be conducted to measure the time gap between emissions from the Oltchim and their deposit in the Olt.

For the measurement of the emissions of Aldehydes out of the chemical plant there exist appropriate analytical methods, but no standardized method for sampling. Because the aldehydes have, depending on the matrix in which they occur, gaseous, adsorbed at particles or dissolved in droplets, different toxic potential it is desired to capture the aldehydes according to their phase. For measuring imissions Denuders are used successfully since a long time. The principle is based on the fact that within a laminar flow gases diffuse based on their high coefficient for diffusion faster lateral to the flow than particles.

Fig. 1: Sampling points for the water analysis.



The effectiveness results out of the big change of the coefficient of diffusion by only small change of the particle diameter. At two particles with a diameter of 1 nm and 10 nm the coefficient of diffusion of the smaller particle is 100 times higher. Coating the surface of the Denuder so that the analyte will be adsorbed selectively, not adsorbed or dissolved substances can be separated. The particles and droplets can pass the Denuder unhindered and can be captured with a filter.

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

5. CONCLUSIONS

Results of the measurements will show if there is a significant contamination of the Olt with aldehydes and to what extend this contamination is related to the industrial production of Oltchim. 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 prioritised by EU-directive 2455/2001/EG.

The economic crisis will open up similar chances for other substances and in other locations as well.

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