Research on monitoring of the emitted aldehydes from a fixed source in the water course

O.Pfann, C. Badaluta Minda, Gh. Cretu

Abstract— The mass amount of industrial emissions of Volatile Organic Compound's (VOC) is very small compared to other pollutants like sulphur, heavy metals, dust or oil. But due to the reactivity even a small amount of organic compounds can have a significant effect on water and air pollution. Denuders are used since long time in air quality analysis as a sampling tool for VOC's. Lately denuders have also proven to be useful for sampling organic compounds in water. The biggest chemical complex in Romania operates a prominent Oxo-Alcohol and causes significant emissions of aldehydes. The paper shows the theoretical basis of the use of denuders and why aldehydes are a relevant pollutant in air and water. Denuders are used in a study to investigate the relation between emissions of aldehydes from a chemical complex and the relevant imissions in the river Olt.

Keywords**—** Volatile Organic Compounds, Aldehyde, Denuder

I. INTRODUCTION

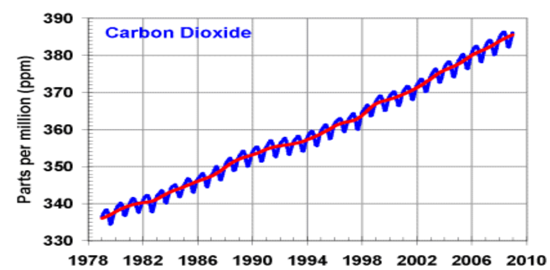
Together with the industrial development the awareness of the Romanian society for environmental protection has increased steadily. "Visible" pollution like smoking exhaust gases, smell in the air or litter pollution of surface water has raised most of the public concerns so far. Until the 1960s only dust-, sulfurdioxid- and nitrous oxide emissions have been considered. Since then a number of VOC's (Volatile Organic Compounds) like aldehydes, amines and cyclical hydrocarbons have been added to the list of monitored substances. These substances are dissolved easily in water or get adsorbed at particles. The chemical reactions of these substances are difficult to be monitored. That's why the primary emissions should be monitored at first hand.

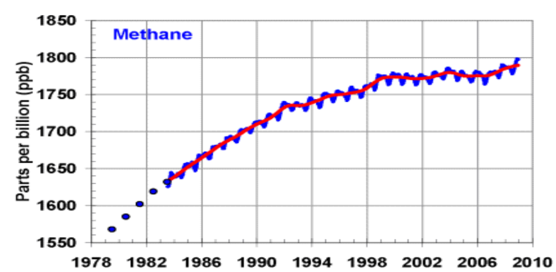
Denuders shall be used to sample both, direct emissions of aldehydes and the imissions into the river Olt. To sample directly at the production site a new sampling device has to be constructed. For constructing this device the high temperature, moisture and particle content in the exhaust gas of the Oxo-Alcohol production has to be considered.

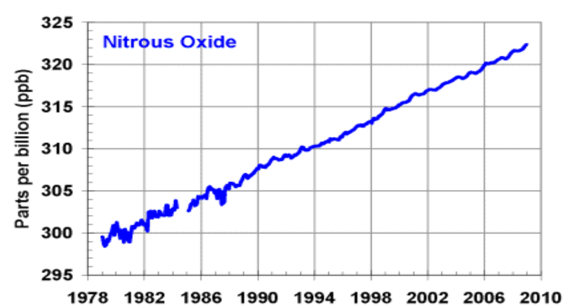
In parallel the corresponding emissions in the river Olt are measured using denuders as sampling device. The idea is to get a direct correlation between the operation of the chemical complex and the pollution of the river Olt with aldehydes.

II. BACKGROUND

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 concentration in the air of none of these substances could be reduced during the last decades (see Fig. 1-3).







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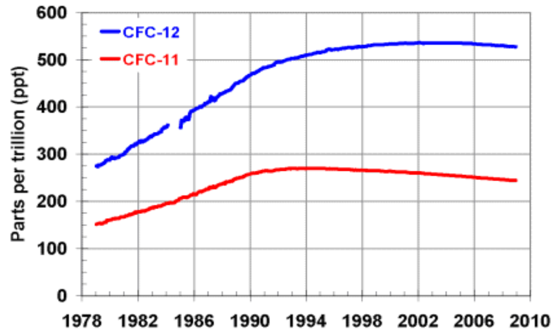


Fig. 1 evaluation of CO_2-content in atmosphere

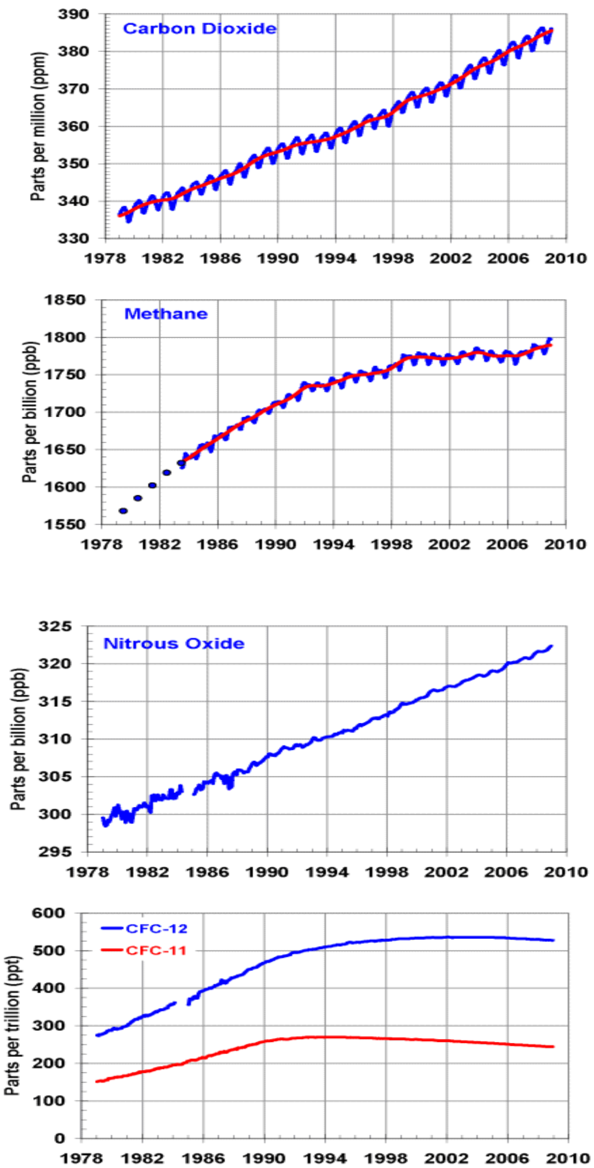


Fig. 2 evaluation of Methan-content in atmosphere

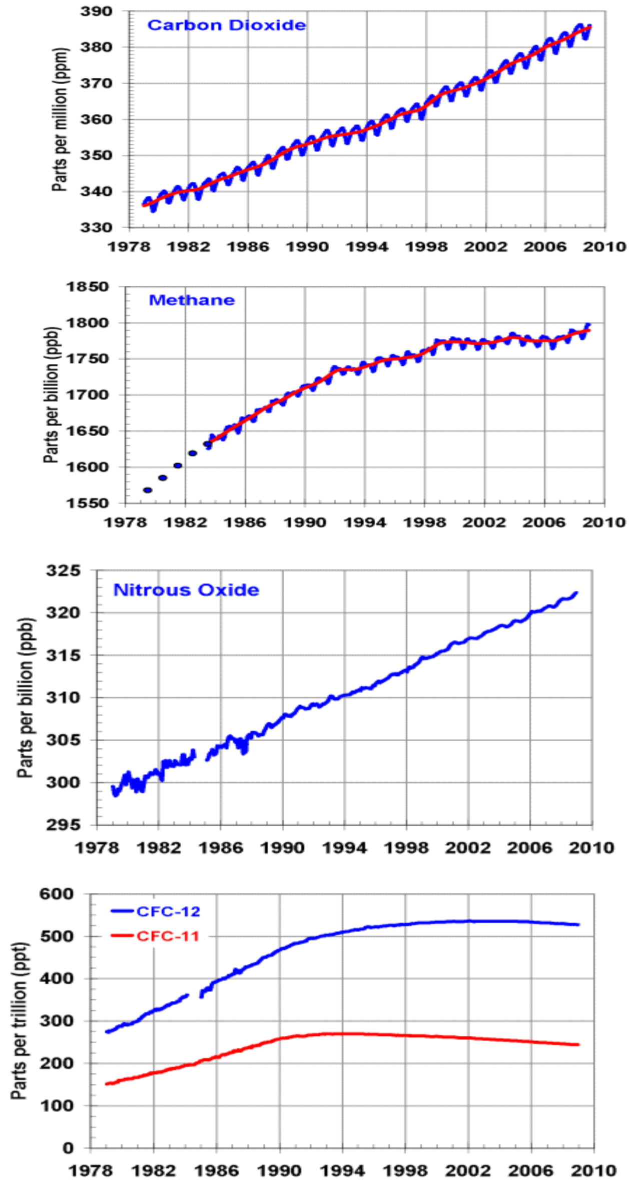
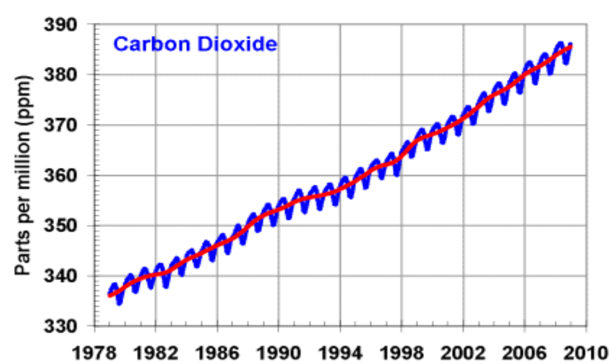


Fig. 3 evaluation of NOX-content in atmosphere



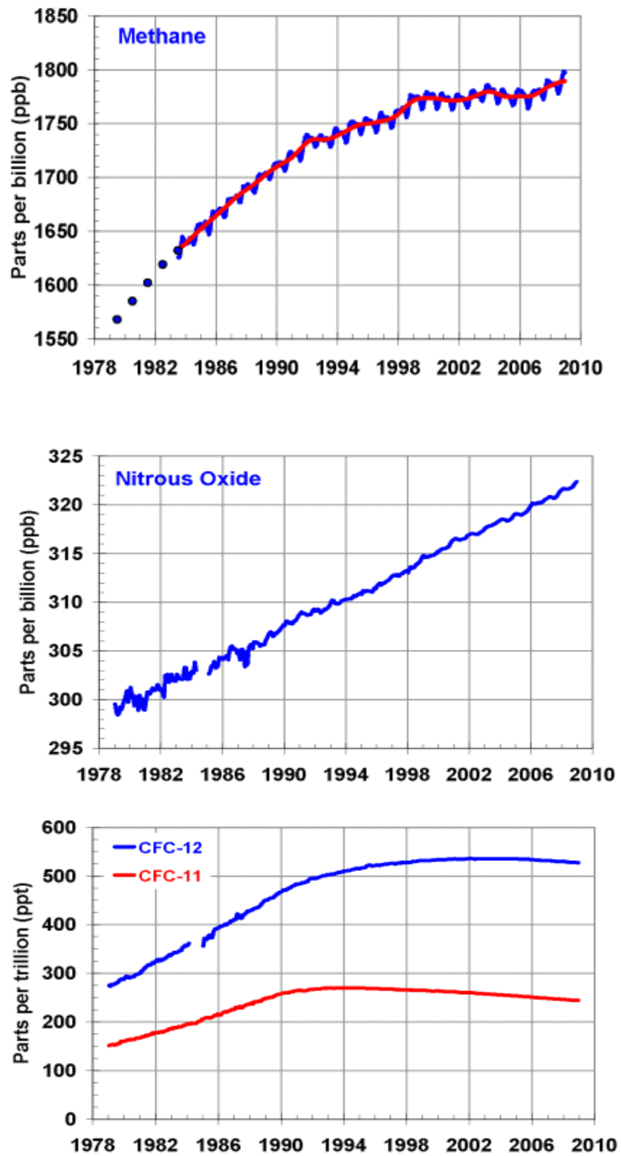


Fig. 4 evaluation of Hydrocarbon-content in atmosphere

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).
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. [1]
Aldehydes are formed through oxidation of primary alcohols. An oxidation means the substitution of 2 hydrogen atoms. This reaction has also leaded to the name for the aldehydes: („Alcohol dehydrogenatus“). Following common particular characteristics in the molecular structure aldehydes can be divided into different groups:

Table 1 groups of Aldehydes

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. [8]

Table 2 aldehyde emissions

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 Formaldehyde 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 exists more detailed data, such as Formaldehyde which has the following effects:

Table 3 effects of exposure to 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

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 river Olt will allow conclusions in regard to the chemical effects happening. The following aldehydes 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 River and directly after the city the effect of a locality 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.

III. EXPERIMENTAL

To capture emissions of volatile organic compounds Denuders are used successfully since a long time. The principle is based on the fact that within a laminar flow small particles and gases diffuse faster lateral to the flow than bigger particles due to the higher diffusion coefficient. At two particles with a diameter of 1 nm and 10 nm the diffusion coefficient of the smaller particle is 100 times higher. If you coat the surface so that analyze is adsorbed selectively organic compounds can be separated from the flow. By this is built up a concentration gradient [2, 3] that keeps the diffusion to the denuder walls running (Fig. 5).

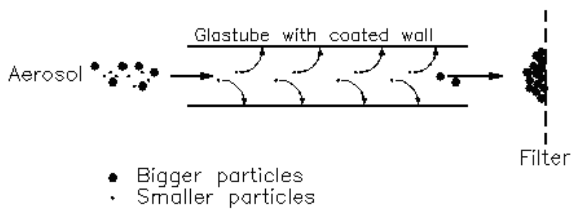


Fig. 5 diffusion of particles

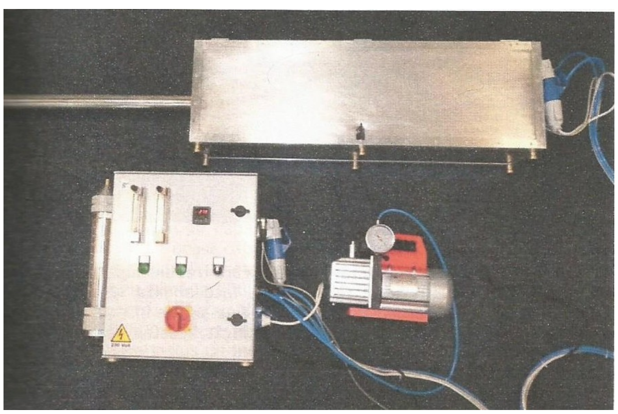


Fig.6 sampling tool

The diffusion can be described with the kinetic theory. Main influence factors are temperature and mobility of the particles[3]

$$D = k \cdot B \cdot T \qquad (1)$$

Where: D - Diffusion coefficient

k: Boltzmann constant ($1{,}38 \cdot 10^{-23}$ J/K)

T: Temperature

B: Particle mobility

And

$$B = \frac{1 + A \cdot (\frac{\lambda}{r}) + Q \cdot (\frac{\lambda}{r}) \cdot \exp(-b \cdot (\frac{\lambda}{r}))}{6 \cdot \pi \cdot \tilde{n} \cdot r} \qquad (2)$$

Where: A, Q, b - Empiric constants

r -Particle radius

λ- Avg. free space

$\tilde{n}$ - Viscosity of the medium

As you can see from the equation the particle mobility and by this the diffusion coefficient increases with reduced particle radius. The equation is valid for particles < 2 µm and only at laminar flow, this means a Reynolds-coefficient below 2000. At a turbulent flow the lateral move is motivated by the flow rather than by diffusion. With known diffusion coefficients the adsorption efficiency can be defined. In Figure 7 the adsorption efficiency of a 50 cm long tube with a diameter of 0,6 cm and a flow of 40 l/h can be seen.

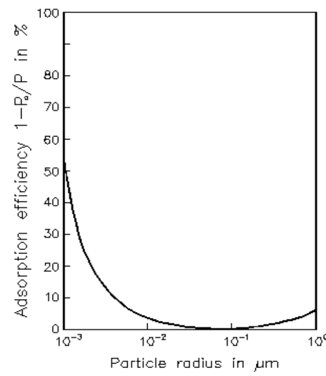


Fig. 7 adsorption of particles in a tube [6]

It can be clearly seen that the adsorption decreases by particles with bigger radius and is then increasing again. This increase is due to sedimentation and can be calculated as follows [7]

$$\frac{N_e}{N_0} = 1 - \frac{2}{\pi} \cdot (2 \cdot \Theta \cdot \sqrt{1 - \Theta^{\frac{2}{3}}} + \arcsin \Theta^{\frac{1}{3}} - \Theta^{\frac{1}{3}} \cdot \sqrt{1 - \Theta^{\frac{1}{3}}} \qquad (3)$$

With

$$\Theta = \frac{3 \cdot v_s \cdot l}{4 \cdot d \cdot \overline{w}} \qquad (4)$$

Where: v_s - sedimentation speed

l: Tube length

d: Tube diameter

$\overline{w}$: Avg. linear speed

Bigger particles can be either separated before or the denuder has to be mounted vertical to avoid unwelcome mass loss.

At the river Olt have been selected 4 measuring points within a distance of 20 km. 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 river Olt will be measured. Therefore in December, when planned restart is carried out, similar measures will be conducted to measure the time gap

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between emissions from the pollutant and their deposit into the river 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.

Also for the ongoing analysis of the samples of water from the River 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.

IV. RESULTS. CONCLUSIONS

Daily measurements throughout the year 2010 have shown the following emissions of aldehydes from the chemical complex:

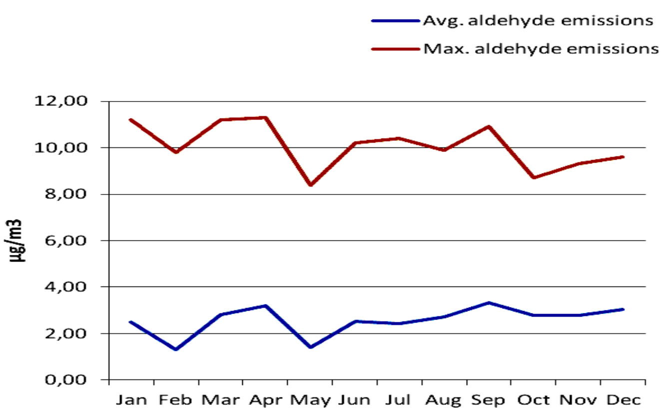

Fig. 8 aldehyde-emissions in µg/m3

During September and August 2010 a total number of 120 samples have been taken from the river Olt to see if there can be detected a contamination with Aldehydes. Following Aldehydes have been considered in the analysis: Formaldehyde, Acetaldehyde, Propionaldehyde, Hexanal, Aceton, Benzaldehyde, Decanal, Furaldehyde. All the analysis done so far show that the content of all aldehydes in the Olt is currently below the detection limit of 400 µg/dm^3.

It is shown that other aldehyde sources like traffic or combustion processes have no significant effect and no imissions in the river Olt could be proven. In order to exclude any mistake in the sampling process or the analysis a double check with an external laboratory from Germany has led to the same results.

It has to be considered that the heating season in winter had not started when the sampling in the river Olt was carried out.

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.

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