

# AIR & BIOGAS



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<http://www.iopan.gda.pl/MarPoLab/>



Wetlands  
Algae  
Biogas



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# AIR

The Earth is surrounded by thin, in comparison with its dimensions, layer of air called atmosphere (gr. *atmos* = gas, mist and *sphaira* = sphere, layer (Phot.1). Due to the atmosphere the sky during the day has a beautiful blue colour, without it would be black. The lowest and the most thick layer of atmosphere is the one in which we live, it is 15 km thick and is called troposphere.



Phot. 1. The Earth with visible atmosphere (satellite picture from NASA, courtesy of Remote Sensing Laboratory of IOPAN)

## Air composition

The air is a mixture of colourless odorless gases, mainly nitrogen ( $N_2$ ) and oxygen ( $O_2$ ) (Fig.1)

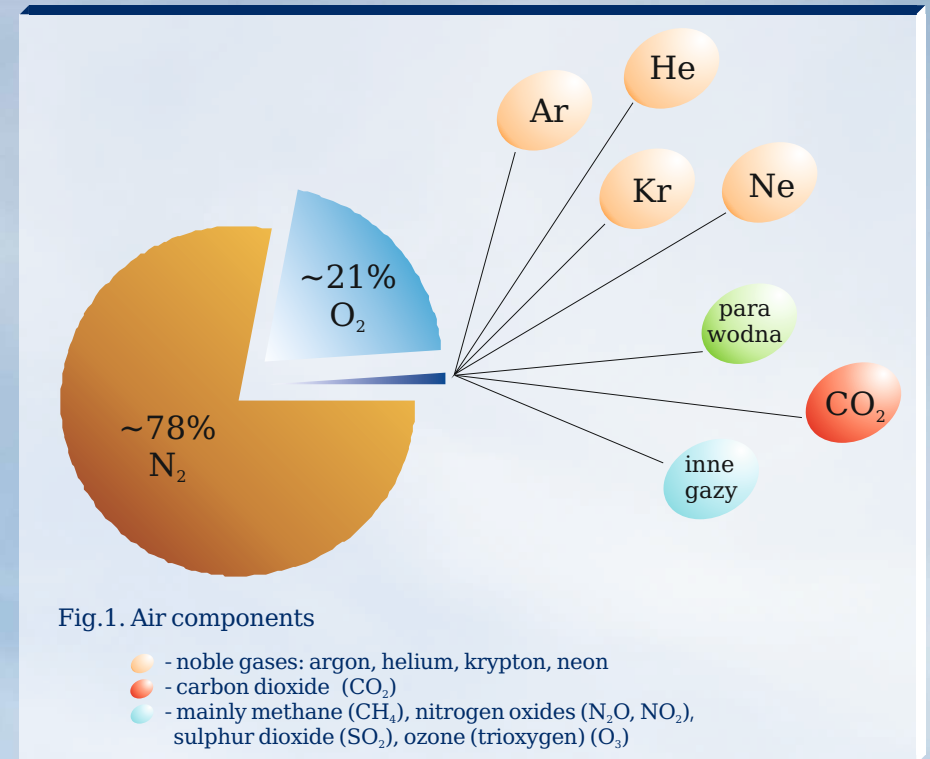


Fig.1. Air components

- noble gases: argon, helium, krypton, neon
- carbon dioxide ( $CO_2$ )
- mainly methane ( $CH_4$ ), nitrogen oxides ( $N_2O$ ,  $NO_2$ ), sulphur dioxide ( $SO_2$ ), ozone (trioxygen) ( $O_3$ )

In the air may also be:

- > water in liquid phase (clouds or mists);
- > matter in the solid phase (soil particles, crystals of salt, volcanic dust), microorganisms, plant and fungi spores.

# Air pollution

In the air pollutants may also occur (Tab.1), i.e. elements, chemical compounds and solid particles, which get into the atmosphere in result of human activities and therefore changing in negative way its natural properties (*Convention on long-range Transboundary Air Pollution*, Geneva 1979).

## Air pollutants may be:

- in gaseous state, e.g. chlorine ( $\text{Cl}_2$ ), ammonia ( $\text{NH}_3$ );
  - in liquid state, e.g. drops of petroleum and its derivatives, drops of solutions containing pesticides;
  - in solid state, e.g. soot particles;
  - aggregates of mixed states of matter;
- 
- primary – such as get into the air;
  - secondary – originating from different processes, e.g. photochemical reactions;
- 
- produced by man, which are not natural, e.g. freons (CFC), artificial radionuclides, e.g. Cs-137;
  - resulting from human activity, but also natural processes, e.g. carbon dioxide ( $\text{CO}_2$ ), methane ( $\text{CH}_4$ ), sulphur dioxide ( $\text{SO}_2$ ), nitrogen dioxide and suboxide ( $\text{NO}_2$  and  $\text{N}_2\text{O}$ ), ozone ( $\text{O}_3$ ).

# Air pollution sources

The sources of the air pollution may be local (e.g. chemical plants emitting gases and dust). However, the most important, in the global scale, is combustion of different fossil fuels for industrial, municipal and transport purposes, burning of garbage and wastes (especially plastics), self-ignition of waste-heaps on landfills, odours from sewage treatment plants.

Tab.1. Examples of air pollutants

Pollutants	Properties
sulphur dioxide ( $\text{SO}_2$ ); product of combustion of fuels containing sulphur; in the air it oxidizes to $\text{SO}_3$ (with water is forming sulphuric acid)	$\text{SO}_2$ – colourless gas of strong-, suffocating-smell, toxic, bactericidal and fungicidal $\text{SO}_3$ – white fumes
nitrogen oxides ( $\text{N}_x\text{O}_y$ , $x,y=1, 2$ ); oxide – NO quickly oxidizes to dioxide – $\text{NO}_2$ , cause so called smog	$\text{NO}_2$ – brown-coloured gas of strong-smell similar to chlorine, strong poison
carbon monoxide (CO), product of incomplete combustion	colourless gas, odourless, forms strong complex with haemoglobin
polycyclic aromatic hydrocarbons (PAHs), e.g. benzo(a)pyrene, products of incomplete combustion	compounds in the solid phase at room temperature, in air – suspended in drops of petroleum products or bound with soot, ash, cancerogenic
ozone ( $\text{O}_3$ )	colourless gas, of fresh smell of the air after storm, toxic, bacteriacidal, used for disinfection
dusts of different origin	depend on origin and chemical composition



The most toxic, mutagenic and carcinogenic compounds, in that dioxines and furanes, are formed during combustion of plastics (e.g. plastic bottles, wastes of laminates, painted and plastic window frames) and impregnated timber wastes, cardboards, illustrated magazines. Examples of compounds, which are generated during burning of plastics, besides CO<sub>2</sub>, CO and NO<sub>2</sub>, are given in Table 2.

Tab. 2. Products of decomposition and burning of plastics - examples

Plastic	Products of decomposition and
polyvinyl chloride (PVC)	hydrogen chloride (HCl), dioxins, furans, vinyl chloride (CH <sub>2</sub> =CHCl) aromatic hydrocarbons
polyurethane (PU)	diisocyanide, hydrogen cyanide (HCN)
polyamide (PA)	hydrogen cyanide (HCN)
polystyrene (PS)	monomers, dimers and trimers of styrene
polyethylene	ethylene (CH <sub>2</sub> =CH <sub>2</sub> ), hydrocarbons

Inhalation of fumes generated during lighting and burning of plastics may cause acute poisoning or even death, already after few minutes. Burning of plastics in individual house hearths and in the open air is causing at least 1000 times higher emission of toxins than their burning in incineration plants.

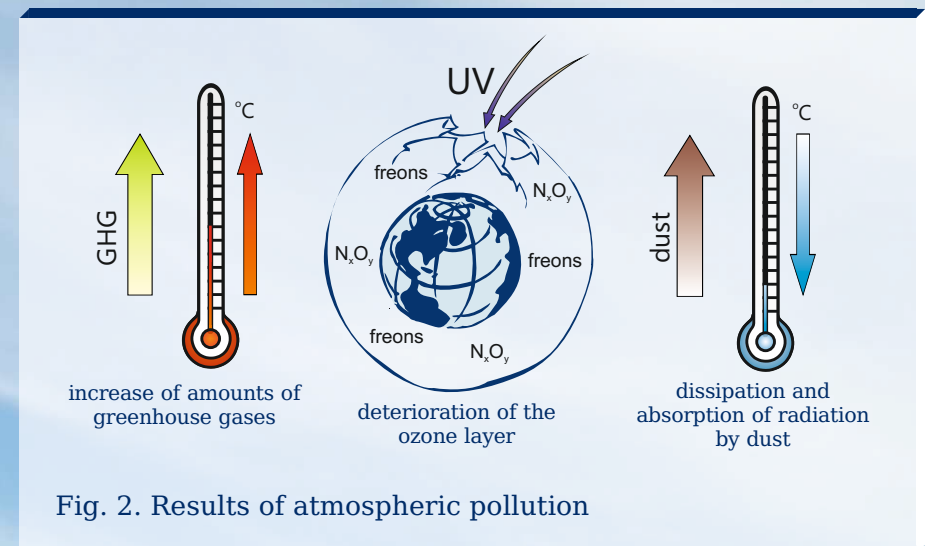
## Effects of air pollution

Diverse and complicated processes which take place in the atmosphere have a fundamental impact on the climate and life on the Earth.

### Influence on climate

Climate of the Earth is influenced by, among others, greenhouse gases (GHGs), which absorb infrared radiation, and after delay emit it to the environment. Atmosphere acts therefore as a greenhouse – accumulating heat and regulating temperature on the Earth (Fig.2).

The greenhouse effect is a natural phenomenon and the one essential for life on the Earth. It is negative, when the proportions and kind of greenhouse gases are changing and equilibria in the atmosphere becomes disrupted (ICCP, 2007).



Influence of particular greenhouse gas depends on its amount and stability in the atmosphere and also its ability to absorb the infrared radiation. The most important role amongst greenhouse gases is water vapour, because it occurs in highest quantities. Other main greenhouse gases are:  $\text{CO}_2$ ,  $\text{CH}_4$ ,  $\text{N}_2\text{O}$ .  $\text{CH}_4$  is the greenhouse gas, which has an effect more than 20 times, and  $\text{N}_2\text{O}$  more than 300 times stronger than  $\text{CO}_2$ .

### *Influence on health*

Air pollution influences human health (Fig.3). Assuming even that when we breath shallowly, we still during 24 hrs breath in  $\sim 10 \text{ m}^3$  of air, and with it everything that it contains. We are breathing also through our skin, absorbing not only oxygen but also pollutants. Breathing through the nose causes the removal of parts of the pollutants.

The most dangerous dust is that of the diameter smaller than 10  $\mu\text{m}$  ( $\text{PM}_{10}$ ), which penetrates respiratory tract of humans and animals, is clogging up stomata of plants and is transferred over far distances. The smaller dust particles are the easier and deeper penetrative organisms and they travel longer in the atmosphere before they fall down on the Earth. That is why recently the dust of diameter smaller than 2.5  $\mu\text{m}$  ( $\text{PM}_{2.5}$ ) has begun to be monitored, for comparison the mean thickness of human hair is 70  $\mu\text{m}$ .

Air pollution has negative effect on human health, which is proven by more and more wide research, carried on in different places of the world. Especially sensitive to that are children, even before birth, because organism of a child is

developing. Children breathe twice as often and more intensively than adults.

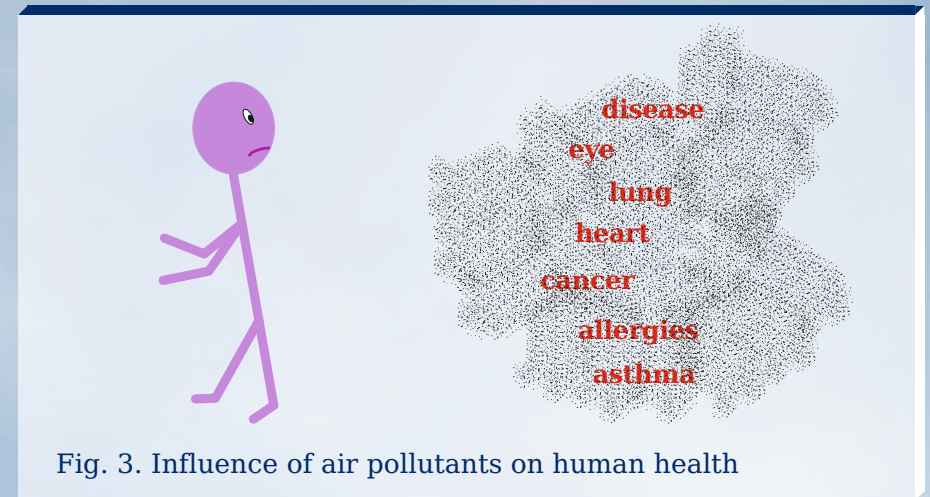


Fig. 3. Influence of air pollutants on human health

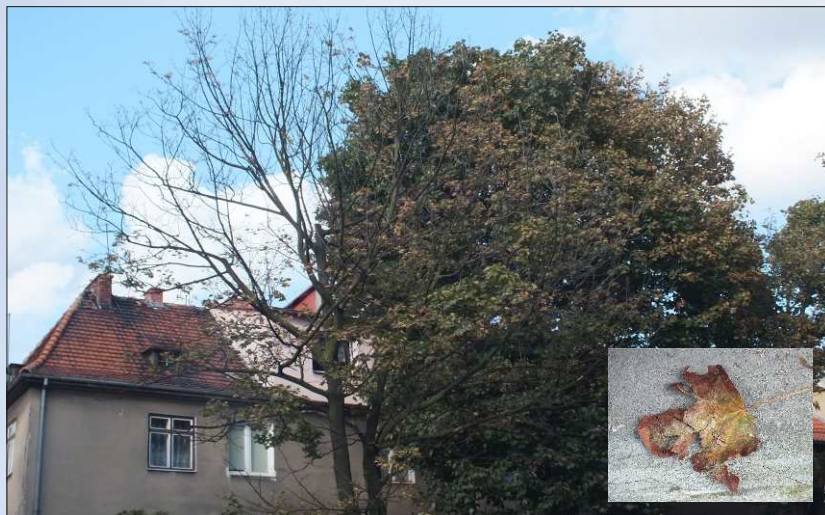
It has been stated that air pollution is considerably more influential than plant pollen in development of asthma, as pollen alone causes this disease very rarely.

Animals and plants are also sensitive to influence of air pollution (Phot.2). For example,  $\text{NO}_2$ ,  $\text{CO}_2$  and  $\text{SO}_2$  are dissolving in drops of water in the air and fall down on the Earth as 'acid rain'. In result, plants turn yellow and die due to the rains acidity.

About 25% of nutrient input comes to the Baltic Sea via the atmosphere. And in eutrophied aqueous basins  $\text{H}_2\text{S}$  (hydrosulphide) and  $(\text{CH}_4)$  are formed (Phot.3).

These are only some selected examples from many possible sources.





Phot.2. Trees at a street of intensive traffic, 6.09.2011

Phot. Marine Pollution Laboratory IO PAN



Phot.3. Results of eutrophication of the Gulf of Gdansk, 7.07.2011.

Phot. Marine Pollution Laboratory IO PAN

## Purification of atmosphere

CO<sub>2</sub> from atmosphere **is removed** first of by **plants**, which in photosynthesis process bound CO<sub>2</sub> and emit O<sub>2</sub>. Plants are also removing other pollutants from the air. Most effective are old trees and phytoplankton in seas and oceans.

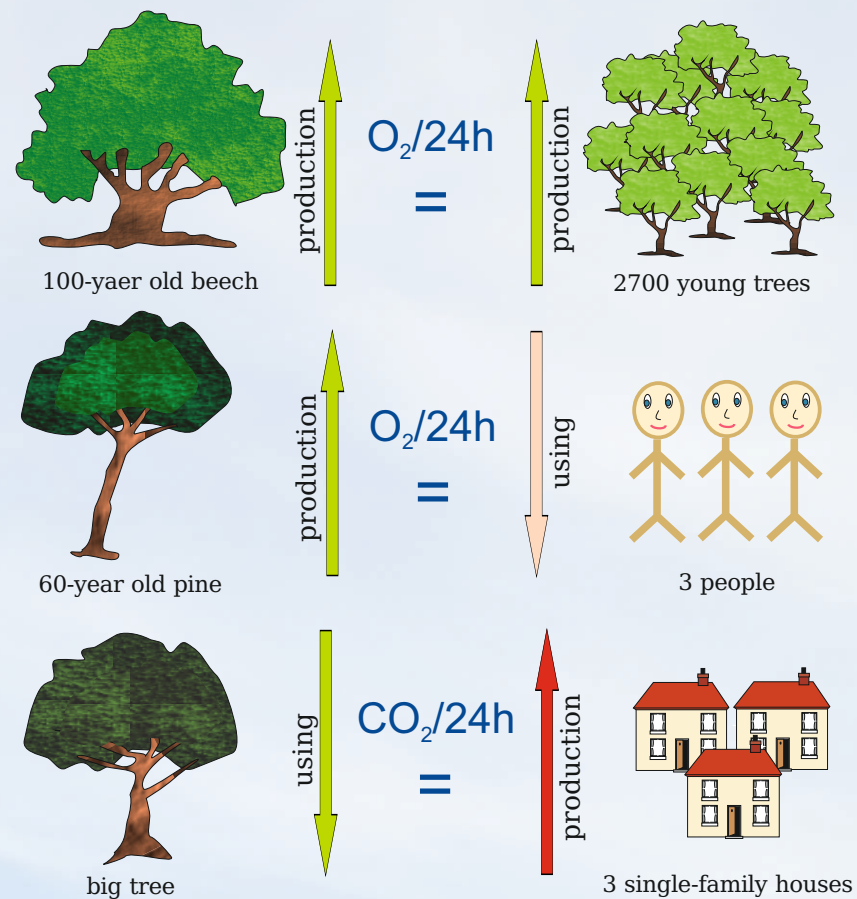


Fig. 4. Participation of trees in purification of atmosphere - examples

According to: Kosmala (2005)

The changing atmospheric system causes not only the transfer but also the concentration of pollutants in some areas.

Pollutants are also removed from the atmosphere together with dry (dust) and wet (rain and snow) fallout. Dust particles are the condensation nuclei, around which water particles gather. Enlarging water drops become more and more heavy and begin to fall down dissolving pollutants and collecting smaller dust particles on their way. Especially effective in cleaning the air is snow, what is visible only when it melts (Phot.4).



Phot. 4. Melting snow, 13.01.2011

*Phot. Marine Pollution Laboratory IO PAN*

## *Legislation - monitoring*

In 1979, in Geneva a convention was signed on long-range transboundary air pollution, which came into a force in 1983. 51 countries have entered into this convention, mainly European (Poland in 1988), but also from North America and Asia. The parties (signatory states) are committed to air monitoring (EMEP - [www.emep.int](http://www.emep.int)).

At present, the Chief Inspectorate of Environmental Protection (GIOS - [www.gios.gov.pl](http://www.gios.gov.pl)), which has its branches in each voivodship (WIOS), is responsible for air monitoring in Poland. They report on the state of the environment, the sources and loads of pollutants and submit data to relevant agencies of EU (European Commission and European Environmental Agency). When the established pollution norms are exceeded, the EU agencies put penalties on such country(s). Poland locates a high position on the list indicating high emission of air pollutants by particular bodies of this convention., e.g. in the recent EMEP Report of 2011 (date from 2009), Poland takes third position after Russia and Ukraine in emission of B(a)P.

In the Pomeranian voivodship air monitoring is carried out also by IMGW (Institute of Meteorological and Water Management) and Foundation ARMAAG (Agency of Regional Monitoring of Air in Gdansk Agglomeration), set up in 1993. At present, the Foundation has 10 monitoring stations on the area of Tricity and Tczew. Due to numerous and often very low concentration, it is impossible to monitor all the possible air



pollutants. That is why, only selected parameters are monitored (Fig.5). On the webpages of ARMAAG Foundation ([www.armaag.gda.pl](http://www.armaag.gda.pl)) and the project AIRPOMERANIA ([www.airpomerania.pl](http://www.airpomerania.pl)) are presented, as up-to-dated, communicates on air pollution, results of concentration of PM<sub>10</sub> (at 2 stations also PM<sub>2.5</sub>) SO<sub>2</sub>, NO<sub>2</sub>, CO and O<sub>3</sub>.

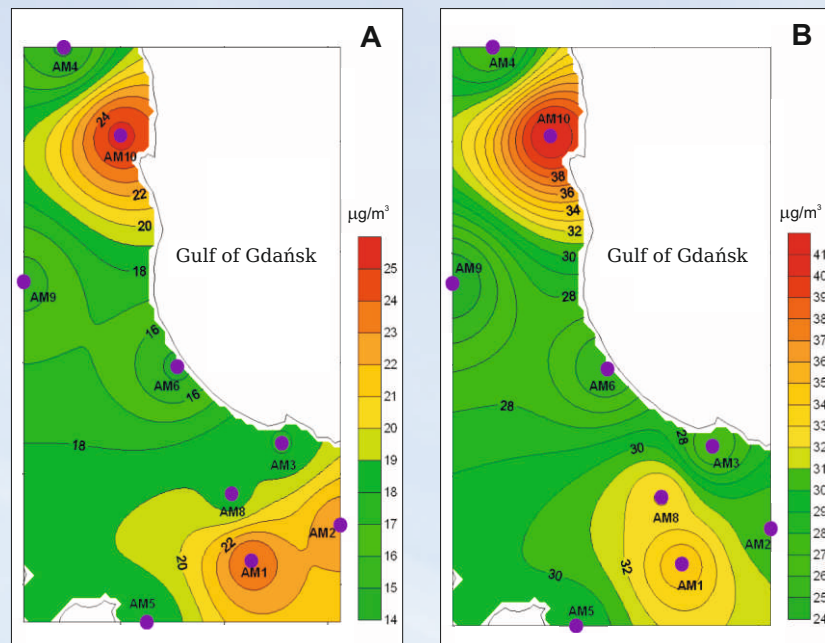


Fig. 5. Concentration of PM<sub>10</sub> (mg/m<sup>3</sup>) on ARMAAG stations (AM1-AM10) in summer (A) and heating season (B), 2010.

ARMAAG (2011)

Measured parameter values are indicators of transport intensity as well as combustion processes, they also depend on meteorological conditions: temperature, wet fallout, speed and direction of wind. That is why the momentary concentrations may differ considerably (Fig. 6).

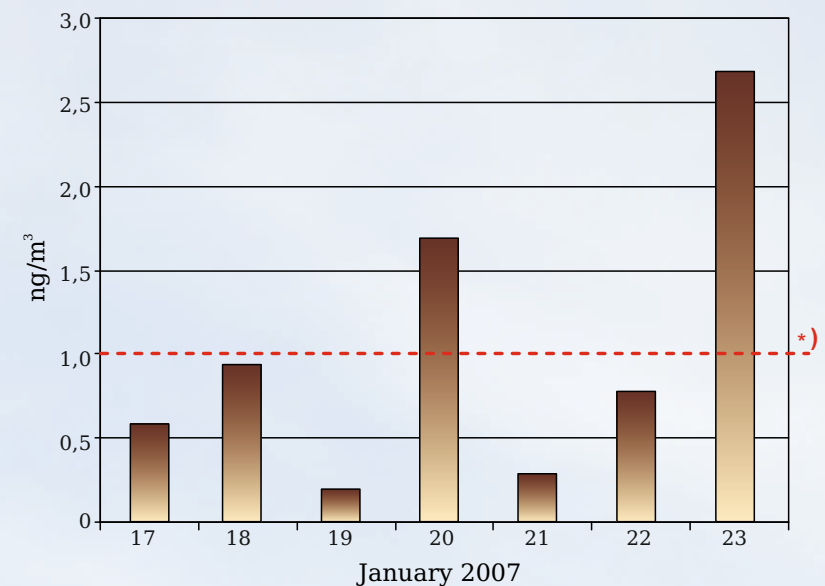


Fig. 6. Mean 24hrs concentrations of benzo(a)pyrene in PM<sub>10</sub>, collected at ARMAAG station (AM6), January 2007.

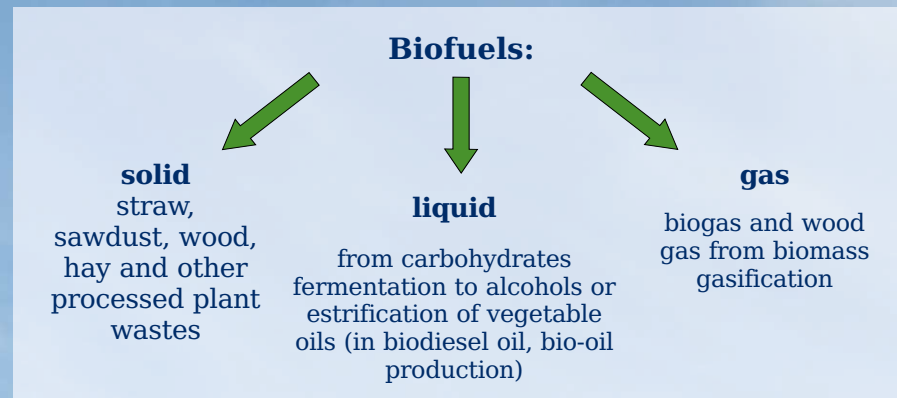
\*) target value (since 2013), averaged for the calendar year, Directive 2004/107/WE (15.12.2004).

According to: Lubecki (2009, 2012).



# BIOGAS

One method of prevention of air pollution is the use of biogas, a sustainable fuel, i.e. a fuel of renewable sources, in contrary to fossil fuels (coal, petroleum), these are natural vegetable and animal originating products or microorganisms, that are used for energy production.



**Biogas** forms during anaerobic (methane) fermentation of organic compounds (proteins, carbohydrates, fats).

These compounds occur in living organisms, but also in:

- wastes of plant and animal origin from the agricultural-food industry;
- municipal wastes and sewage;
- manure;

- plant materials e.g. from maize, but also cultures of unicellular algae and blue-green algae (cyanobacteria), which are very effective biomass for production of biogas.

Process of anaerobic fermentation is a natural one. The formed biogas is slightly heavier than air, consists of methane (50-85%) and carbon dioxide (~15%). Methane at room temperature is colourless, odourless gas; was being called marsh gas or mine gas.

A man has learnt how to reclaim biogas and use it as an energy source (Fig.7). The first installation for biogas production was build at the end of XIX century.

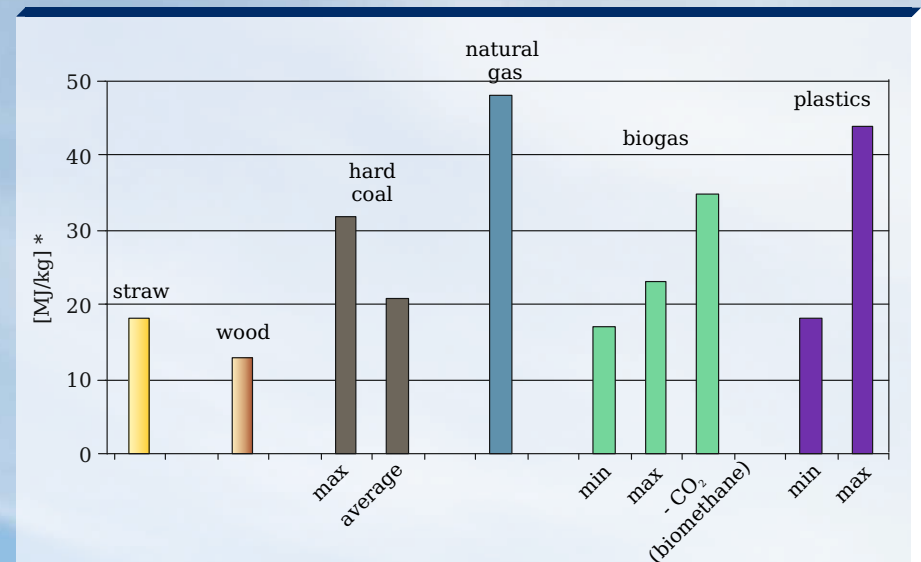


Fig. 7. Heating values of different fuels.

\*) - 1MJ= 0,278 kWh

According to: Lewandowski (2007)

At present, there are biogas works on different technological level, using mainly:

- sediments in sewage treatment plants;
- organic industrial wastes;
- municipal wastes from waste grounds;
- manure and plant biomass (agriculture biogas works).

## *Advantages of biofuel usage*

- decreasing of greenhouse gas concentration: CO<sub>2</sub> and CH<sub>4</sub>;
- limiting of emission of SO<sub>2</sub>, CO<sub>2</sub>, N<sub>x</sub>O<sub>y</sub> and dust;
- obtaining of fertilizer (agriculture gas works).

## *Technological faults*

- untight fermentation tank
  - additional biogas components are nitrogen and oxygen from the air, which is destroying methane bacteria;
- acidification of the fermentation sediment
  - more hydrogen (H<sub>2</sub>) and hydrosulphide (H<sub>2</sub>S) are formed;
- too much protein in the biomass (C:N<100:3)
  - more ammonia (NH<sub>3</sub>) is formed, which is destroying

Hydrogensulfide and ammonium are the toxic gases which in determined proportions make explosive mixtures, like hydrogen and methane.

## *Air pollution matters*

- supplying substrates in not tight containers
- not proper technologies (fermentation process proceeds not uniform and not finalized)
- rapid changes of technology (methane bacteria for proper fermentation need determined conditions of temperature, acidification (pH), sort and proportions of substrates).

That is why it is important to apply **good technologies** and adhere to **technological procedures**.

The sources of air pollution during biogas production might be:

- substrates (supplied in improper way);
- non purified biogas;
- fermentation residues (non full fermentation).

There are fears regarding substrate supply. That is why big biogas works, using municipal and animal originating wastes should be located and supplied with substrates in a well thought-out way, and e.g. in agricultural biogas works different sorts of silages can be used, which smell is not an environmental nuisance.

One should remember also, that sewage treatment plants using aerobic decomposition of organic matter in open tanks,



cattle and pig farming and fertilizing with **untreated manure** cause **greater nuisance** to environment than **biogas works** and fertilizing with **post-fermentation residue**.

Biogas, depending on **sort of biomas**, may contain different pollutants:

- sulphur and chlorine compounds, derivatives of aromatic and aliphatic hydrocarbons, mainly from plastic wastes – mostly in biogas recovered from not sorted municipal waste grounds;
- other volatile sulphur compounds ( $H_2S$  and other) – mostly in biogas from agriculture biogas works, their quantities depend on sort and origin of substrates;
- ammonia – when the biomas contains a lot of proteins, mainly in animal originating wastes
- siloxanes – commonly used in cosmetic industry and for production of cleaner agents, they occur in sewage sediment, do not decompose during fermentation; a part transfers to biogas and the rest stays in fermentation residue; some may cause irritation of the skin, but the most dangerous they may be for engines and turbines.

That is why **purification of the biogas** is necessary before its usage as a **fuel**.

## SUMMARY

The air, similarly like water, is necessary for life. Without it the Earth would be cold, we could not breath, make fire in the oven or drive a car. The plants could not grow nor could animals live, so we would be hungry. So, why do we:

- drive the vehicles which are out of order and let out polluting “black” smoke?
- burn plastics and old tyres?
- do not segregate wastes and dispose them on heaps on waste grounds?
- go out to the fresh air and light a cigarette?
- destroy trees?
- pollute the sea?



Phot.5. Fire, 18.10.2011

Phot. Marine Pollution Laboratory IO PAN

Conviction, that this **what we cannot see does not exist** and if even does, so will be quickly taken away by **wind, is not right**. In the world today more and more pollutants are emitted to the atmosphere, which do not disappear but are transferred sometimes over very far distances, much more easily than pollutants in water.

The results of air pollutions became very important in recent years, which are proven by different international and national **legislation**. Also Polish **administration's have noticed problems** connected with air pollution, though often **investments** connected with improving the air quality are **not sufficient**, and Poland takes high position on the list of countries polluting the air.



Phot. 6. Smoke, 04.04.2011

Phot. Marine Pollution Laboratory IO PAN

However, it most important is that **society** should realize how **important clean air** is for our **existence**, and undertake all the possible activities to improve the situation, while administration's should make these activities easier, for example by creating conditions for using sustainable energy sources, for example **biogas**.

## BIBLIOGRAPHY

- Arnold M., 2009, *Reduction and monitoring of biogas trace compounds*, VTT Research Notes, 2496.
- ARMAAG, 2011, *Stan Zanieczyszczenia Powietrza Atmosferycznego w Aglomeracji Gdanskiej i Tczewie w roku 2010 i informacja o działalności fundacji*, red. K. Szymanska.
- Duxbury A.C., Duxbury A.B., Sverdrup K.A., 2002, *Oceany swiata*, Wydawnictwo Naukowe PWN.
- Glaszczka A., Wardal W.J., Romaniuk W., Domasiewicz T., 2010, *Biogazownie rolnicze*, MULTICO Oficyna Wydawnicza, Warszawa.
- ICPP, 2007, *Zmiana klimatu 2007: Raport Syntetyczny*, red. Pachauri R.K., Reisinger A., Wydawnictwo IOS, Warszawa, 2009.
- *Konwencja w sprawie transgranicznego zanieczyszczania powietrza na dalekie odleglosci sporządzona w Genewie*, 13 listopada 1979 r.
- Kosmala M., 2005, *Po co ludziom drzewa, czyli o roli i znaczeniu drzew w zyciu czlowieka*, Materiały I Konferencji Naukowo-Technicznej: Zielen Miejska. Naturalne bogactwo Miasta. Torun, 3-4 pazdziernika: 7-8.
- Lewandowski W., 2007, *Proekologiczne odnawialne zrodla energii*, WNT, Warszawa.
- Lubecki L., 2009, *Wielopierscieniowe węglowodory aromatyczne w osadach Zatoki Gdanskiej, jako markery roznych zrodel zanieczyszczen tego akwenu*, praca doktorska, Instytut Oceanologii PAN, Sopot.
- Lubecki L., Kowalewska G., 2012, *Suspended PM<sub>10</sub> particles in urbanized coastal zone (Tricity agglomeration, Poland) a possible source of PAHs for sediments of the Gulf of Gdansk*, Polish Journal of Environmental Studies.
- Stanley S.M., 2002, *Historia Ziemi*, Wydawnictwo Naukowe PWN.