# MONITORING OF INDUSTRIAL POLLUTANTS IN OIL AND PETROCHEMICAL INDUSTRY

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Data on industrial monitoring, integral control and pollution prevention in Oil and Petrochemical Industry are presented in the thesis. Industrial monitoring as integral control has the function of pollution prevention. In the thesis we have analysed the measuring results of sulphur dioxide ($SO_2$), nitrogen dioxide ($NO_2$), nitrogen oxide (NOx), ammonia ($NH_3$), ozone ($O_3$), benzene-toluene-xylene (BTX) and total hydrocarbon (THC). Discussion of results shows which places are pollution sources and where we should take action first in order to reduce the pollution. By defining the place of pollution we determine control and pollution reduction measures with the possibility of choosing the type of monitoring and the dynamic of measuring the pollutants.

*Key words*: Emission; Industrial monitoring; Integral control; Pollution.

## INTRODUCTION

Monitoring is a process by which the industry measures its emissions, releases, and/or parametres of its performances that are to provide information on the release of polluting materials and/or performance of control technologies. It provides secret or public information on the nature of pollutants emissions and/or the performance of purification plant. Industrial monitoring of emissions from the industry is performed by the purification plant` s operator, in accordance with appropriate, defined and amended programme for taking samples and in accordance with accepted measuring protocols (standards or analythical methods or evaluation methods). Operators can also hire another laboratory to perform industrial monitoring on their behalf (it should be an accredited laboratory).

Industrial monitoring regimes for integral control and pollution prevention (IPPC) may comprise the following:

C Emission of exhaust gases and flying substances

C Flow of waste water via the sewer system in and from water purification plants, up to the recipient

C Solid waste deposits on depots

C Depositing solid and liquid waste, including the organic waste, in burning rooms

C Industrial treatment of raw materials (such as traces of polluting materials) and conditions in plants (treatment temperature, pressure and flow)

C Diffusive release into the air, water and soil

C Recipients of emissions such as air, grass, surface soil and underground waters

C Expenditure of raw materials and energy

C Sources and levels of noise and vibrations

C Sources of smells

C Conditions in the plant

C Performance and maintenance of monitoring equipment.

Requests for industrial monitoring increase in the following situations:

– Complexity and sensitivity of measuring technics and the rise of prices

– Accepetance of EMAS and ISO 14 000 by the foreign industry
– Implementation of IPPC
– The polluter pays principle is applied, especially in the case of regulatory regime that does not reimburse manufacturers for monitoring
– Manufacturers willingly perform the monitoring or there is an obligation of performance
– Conditions of performing Self-monitoring
– Confidence in the quality of results (QA/QC)
– Application of the standardised measuring methods, where possible (sampling and analysis)
– Certified instruments
– Trained personnel
– Accredited laboratories.

Bases of industrial monitoring in Europe:
– Council Directive 96/61/EC of 24 September 1996 IPPC Directive
– Directive on the limit values from Articles 18 (2) and 20 of IPPC Directive (Annex II IPPC)
– (EC) Regulation No 761/2001 of the European Parliament and of the Council of 19 March 2001, governing EMAS
– IPPC Reference document on the General Principles of Monitoring, November 2002
– BREF's prepared by the European IPPC Bureau – EIPPCB.

### Monitoring Methods

The methods to be applied as necessary can be divided in two basic categories:
– non-continuous
– continuous.

### Non-continuous Monitoring

- The main form is periodical monitoring in regular intervals, in order to include a defined part of the production process or representative time intervals (hourly, daily, monthly, etc.)
- It may include composite samples taken in selected intervals, and sample analysis is cumulative within a specified period, or the data from the instruments are read in regular intervals during the production process. Monitoring periods are determined in advance (in the permit or by the law) and they have to include the entire process
- Each parameter can be analysed in the waste water or waste gas sample, with the gas depending on the collecting equipment such as the filters, impingers, scrubbers, absorbents, etc.

### Continuous Monitoring

- Continuous measuring series ensuring the data in high-resolution time (e.g. constant data collection from the instant feedback instruments).
- Data are frequently available in real time (from electronic monitors) and are useful for process control.
- Continuous measuring may be more expensive compared to the non-continuous one, depending on the frequency of periodical measurings.
- Continuous monitoring of air primarily refers to $SO_2$, NOx, CO, and particles.
- Continuous monitoring of waste water is frequently limited to the flow, pH, electrical conductivity and temperature, as well as to some specific ion fluorides, sulphides, nitrates and cyanides. The other relevant parameters such as the biological consumption of oxygen, chemical consumption of oxygen, nitrogen, phosphates, oils and grease, detergents, heavy metals, pesticides etc., are measured periodically and analysed in laboratory.

### Monitoring Frequency

- Refers to the time between individual measurings or measuring groups.
- Varies in different situations (from once a year to continuous 24-hour on-line measuring).
- Examples of monitoring frequency (the Dutch law on determining the fees for discharging waste waters):
  – Category 1 (small amount): monitoring is not required
  – Category 2 (medium amount): 4–10 mixed, 8–24 hours of individual samples (depends on the production cycle)
  – Category 3 (big amount): 1–4 representative composite samples in a week (per season)
  – Category 4 (big pollutants): continuous monitoring or maximum 12 proportional weekly average values (per season).

Monitoring parameters and testing methods are presented in a BREF document “General Principles of Monitoring”. The relevant EC Directives specify the monitoring methods and standards such as EN-CEN and ISO standards for particular priority parameters. Parameters that for the greatest part of industrial emissions and discharges have to be observed, are listed in the BREF documents.

Relevant air pollutants: sulphur dioxide and other sulphuric compounds, nitrogen oxides and its other compounds (NOx), carbon monoxide, suspended organic compounds, metals and their compounds, dust, asbestos (suspended particles, fibers), chlorine and its compounds, fluorine and its compounds, arsenic and its compounds, cyanides, carcinogenic and mutagenic matter and PCB.

Relevant water pollutants: organohalogenic compounds, organophosphorous compounds, carcinogenic or mutagenic substances, persistent hydrocarbons, cyanides, metals and their compounds, aresenic and its compounds, biocides and plant protecting products, suspended matter, substances contributing to eutrophication (particularly nitrates and phosphates) and the substances having a negative effect on the oxygen balance.

## RESULTS

By way of the passive sampling method, eight measuring campaigns were conducted, useful for analysing:

Campaign 1 (11.08.2005 – 26.08.2005),
Campaign 2 (31.08.2005 – 15.09.2005),
Campaign 3 (20.10.2005 – 04.11.2005),
Campaign 4 (09.11. 2005 – 23.11.2005),
Campaign 5 (17.01.2006 – 31.01.2006),
Campaign 6 (03.02. 2006 – 18.02.2006),
Campaign 7 (20.04. 2006 – 04.05.2006),
Campaign 8 (03.02.2006 – 18.02.2006).

The measured quantities have graphically been presented per inorganic components (sulphur dioxide $SO_2$, nitrogen dioxide $NO_2$, total nitrogen oxides NOx, ground-level ozone $O_3$, ammonia $NH_3$) and per organic components (benzene, toluene, xylene and total hydrocarbons). There are 35 measuring places and these present the town and industry effect zones (Fertilizer plant, Petrochemical plant and Oil Plant).

Effect zone Fertilizer plant presents measuring places under number (10-19). Effect zone Petrochemical plant presents measuring places under numbers (19–22). Effect zone Oil Plant presents measuring places under numbers (22–35). Figure 1 shows that the greatest measured value for sulphur dioxide $SO_2$ is in campaign 5, then in campaign 4, and the lowest in campaign 1. Figure 2. shows that the greatest measured values for nitrogen dioxide are in campaigns 7 and 3, but a trend of constantly highest measured values of nitrogen dioxide in certain measuring places (7, 13, 21) can be noticed. The lowest values were measured in campaign 8. Figure 3 shows that the highest measured values of the total nitrogen oxides NOx are in campaign 3, and the lowest in campaign 1. Figure 4 shows that the highest measured values of the ground-level ozone $O_3$ are in campaign 8, and the lowest in campaign 4. Figure 5 shows that the highest measured values of ammonia $NH_3$ are in all campaigns in measuring places 21 and 23. The greatest value is in campaign 1, and the lowest in campaign 8. Figure 6 shows that the highest values of the total hydrocarbons are constantly measured at the measuring places from 31 to 35.

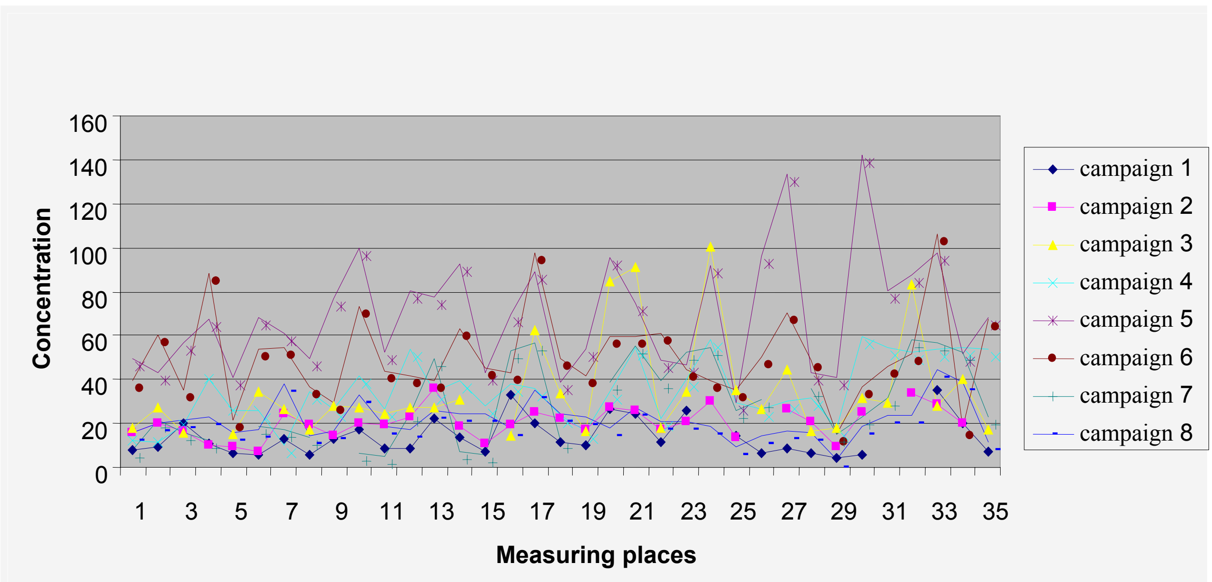


Fig. 1. Graphic presentation of sulphur dioxide $SO_2$.

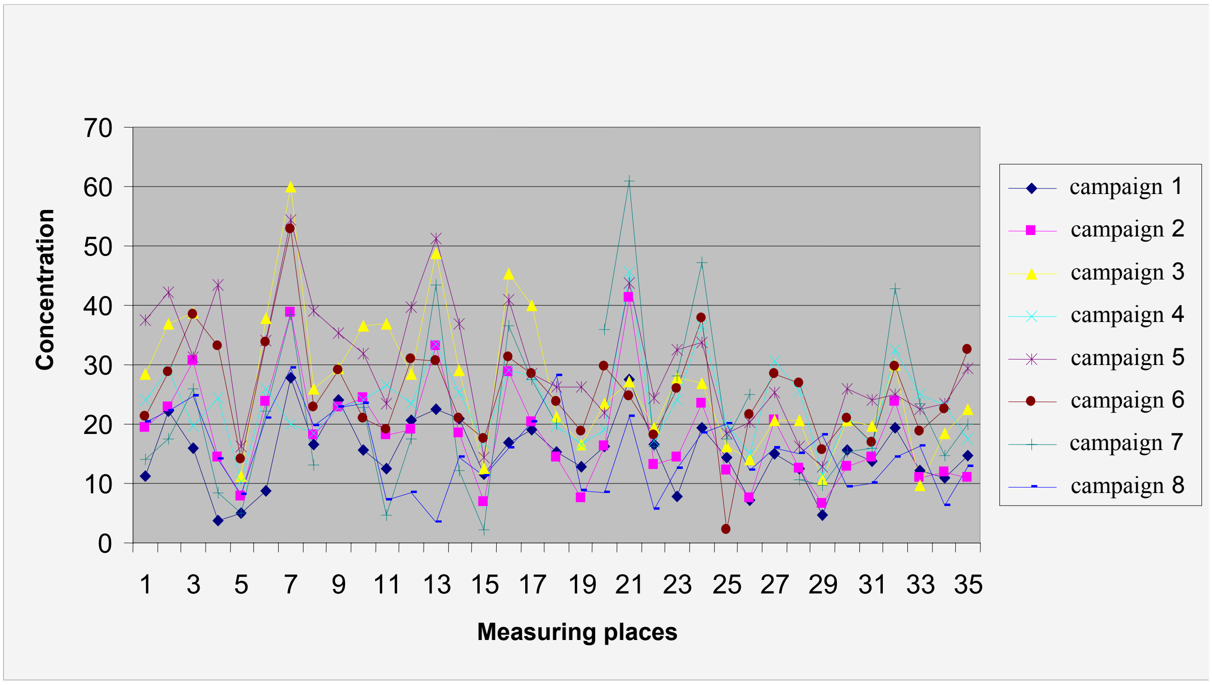


Fig. 2. Graphic presentation of nitrogen dioxide $NO_2$.

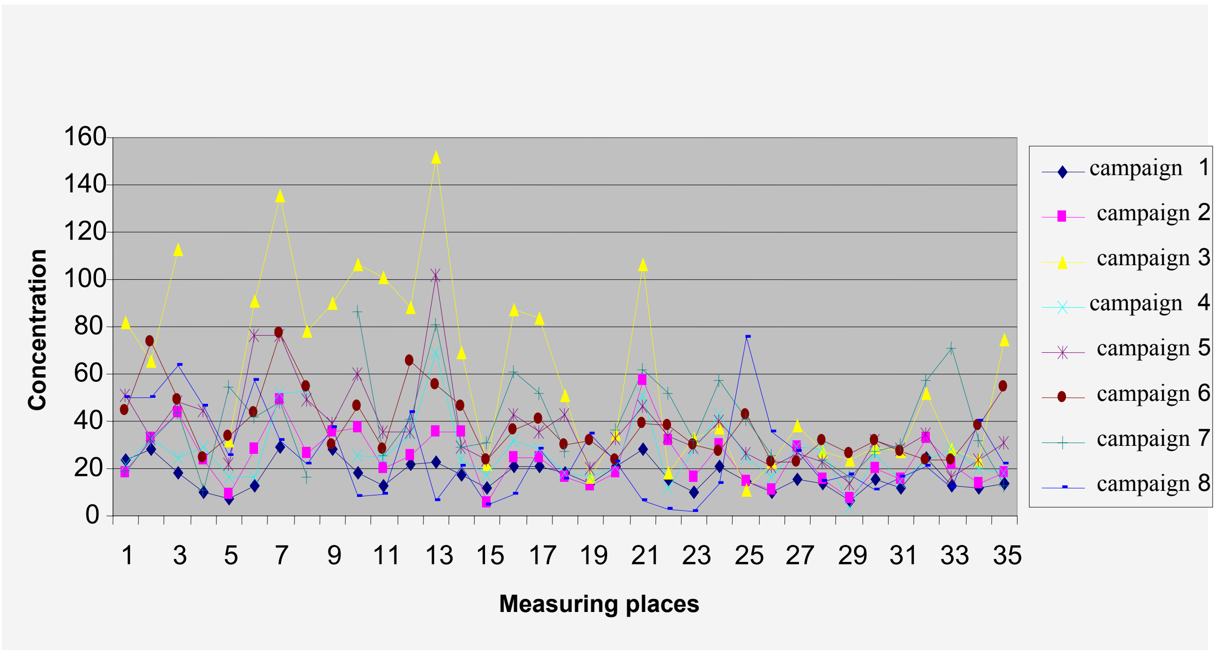


Fig. 3. Graphic presentation of the total nitrogen oxides NOx.

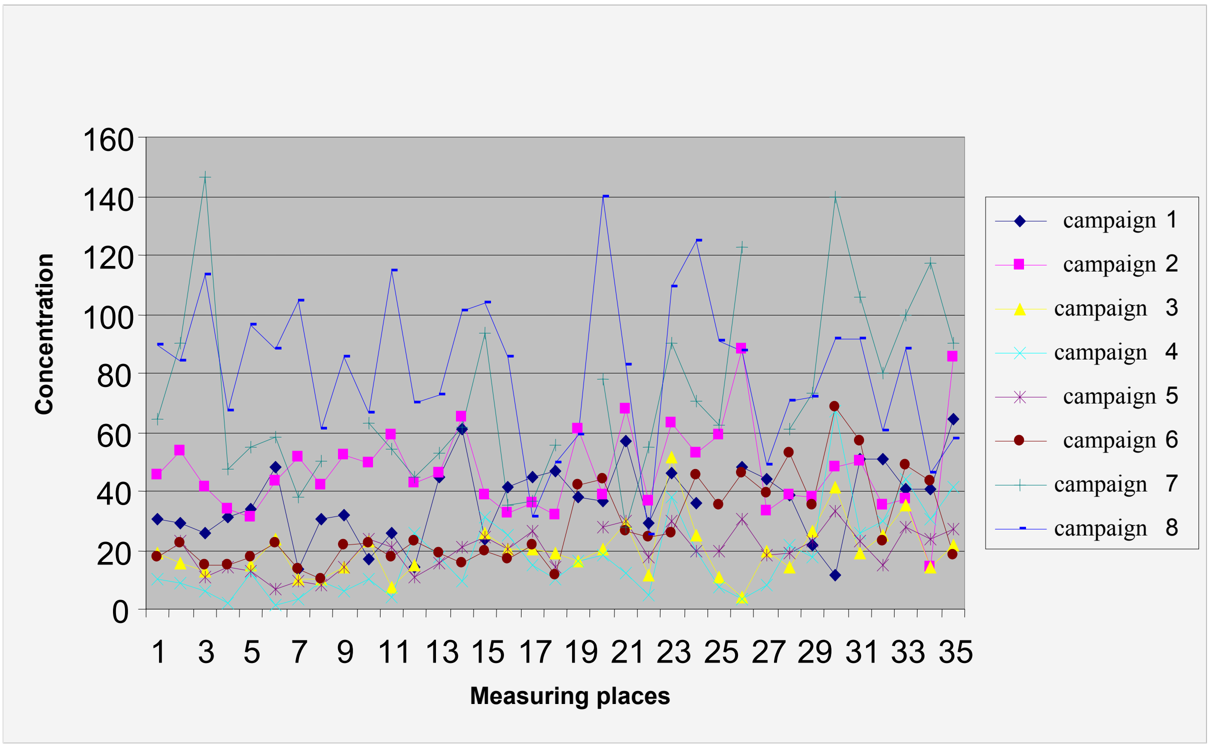


Fig. 4. Graphic presentation of ozone $O_3$.

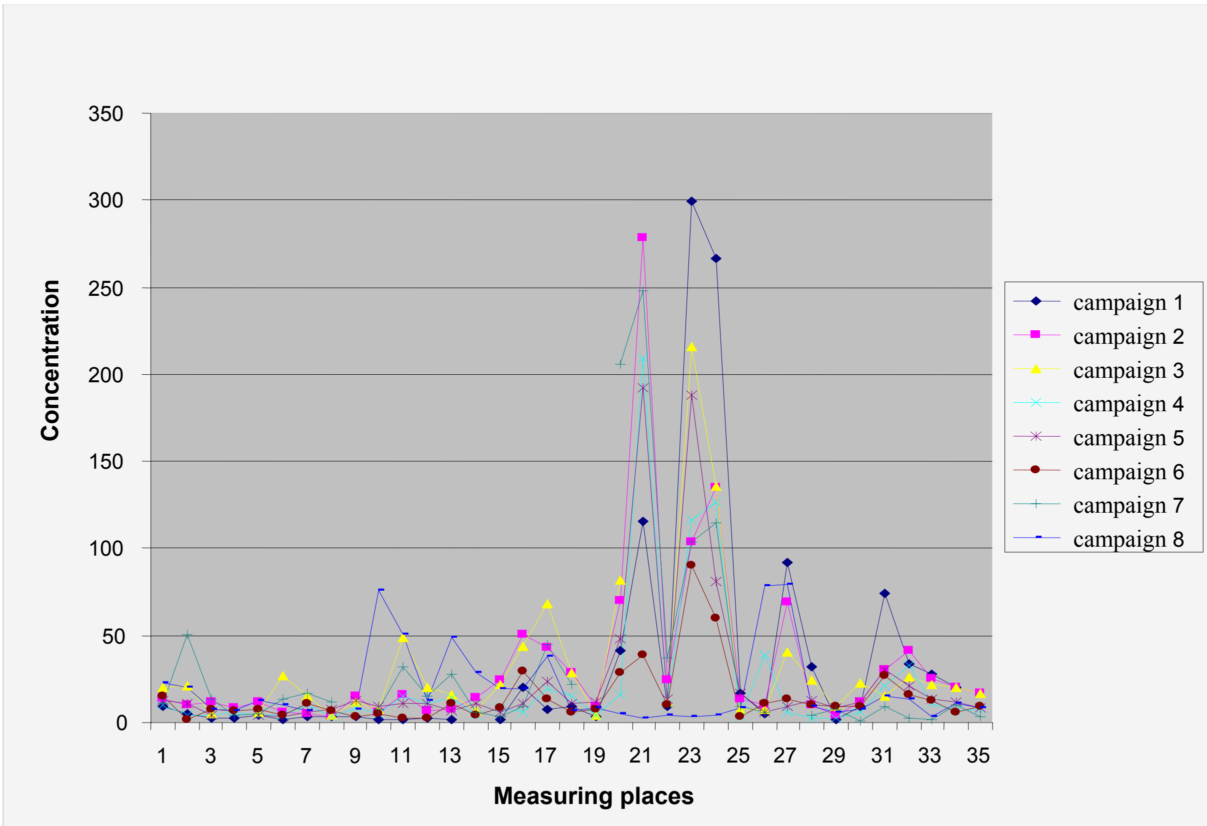


Fig. 5. Graphic presentation of ammonia $NH_3$.

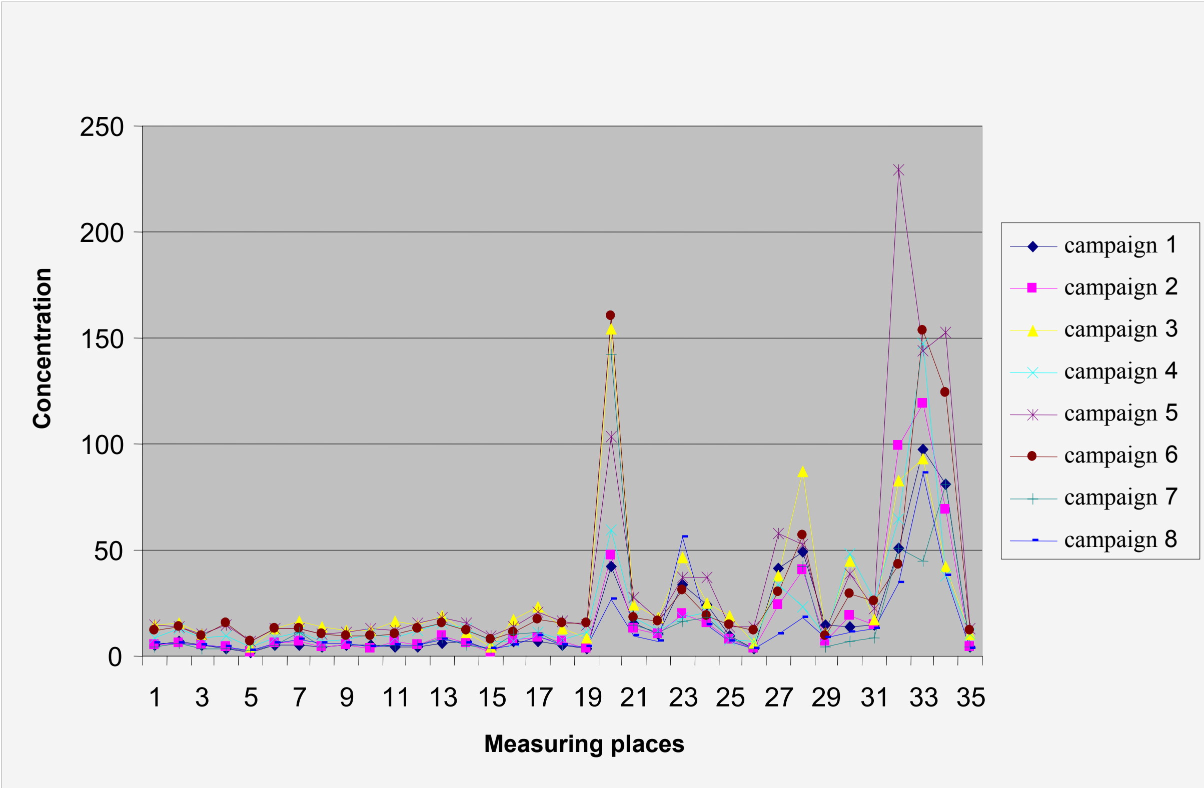


Fig. 6. Graphic presentation of benzene.

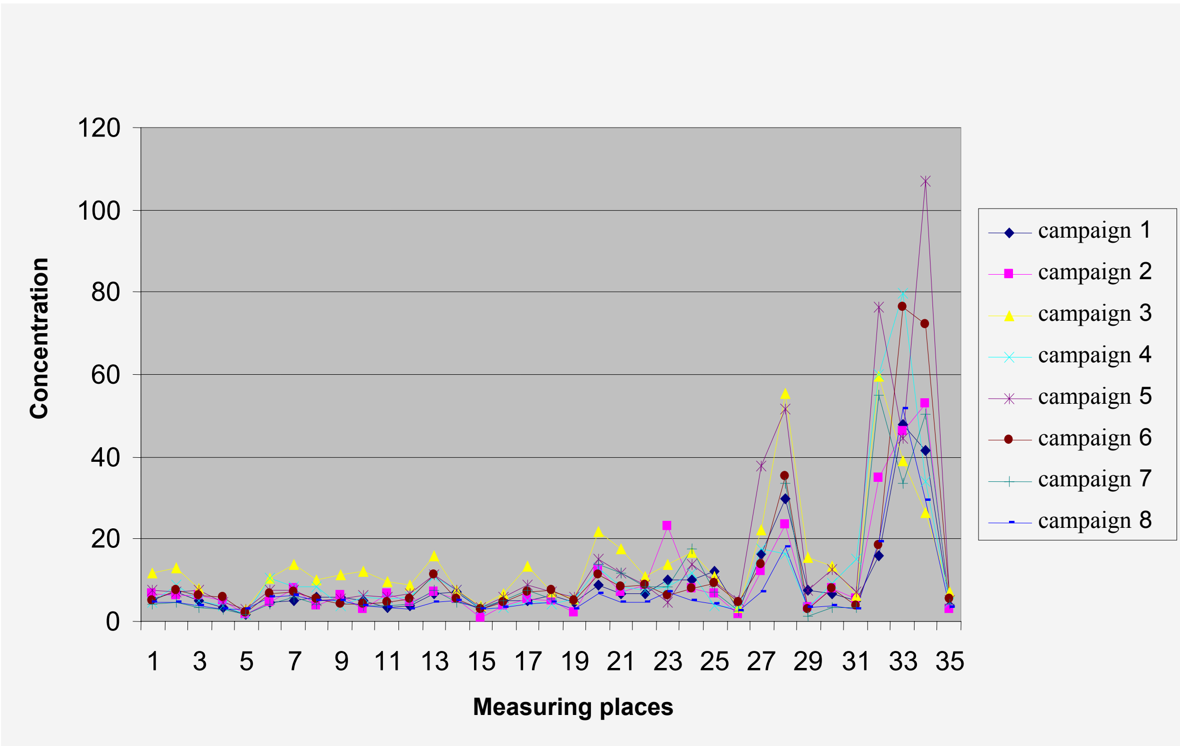


Fig. 7. Graphic presentation of xylene.

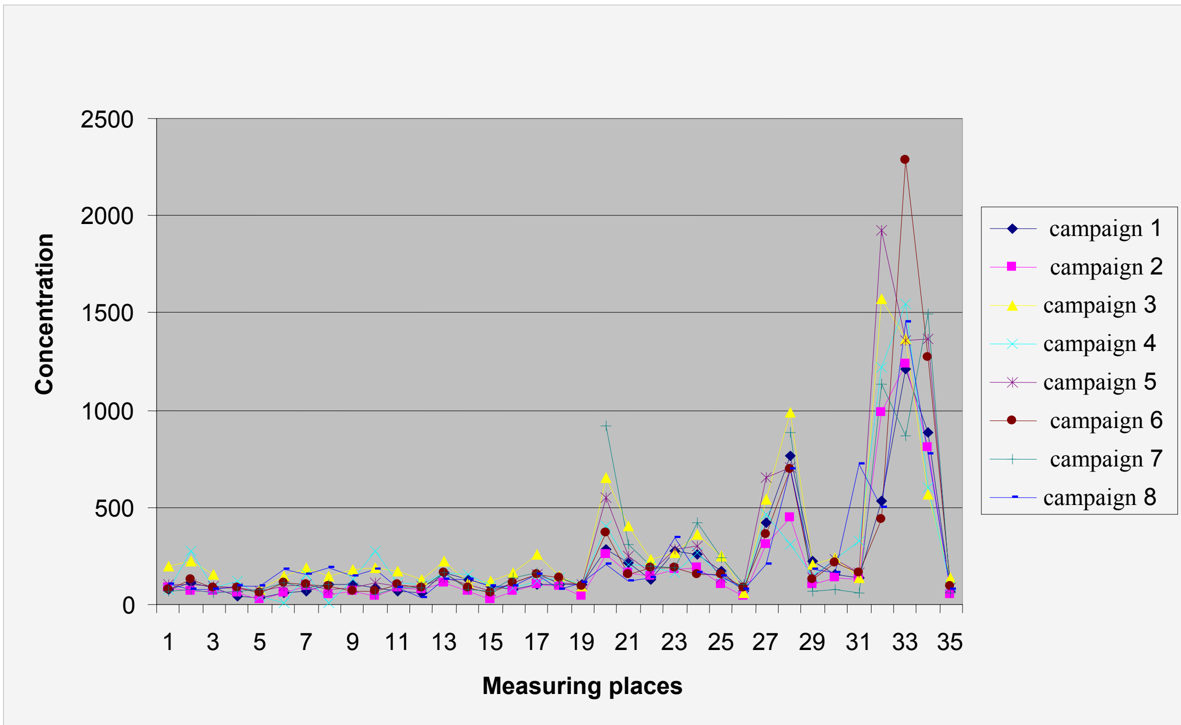


Fig. 8. Graphic presentation of the total hydrocarbons.

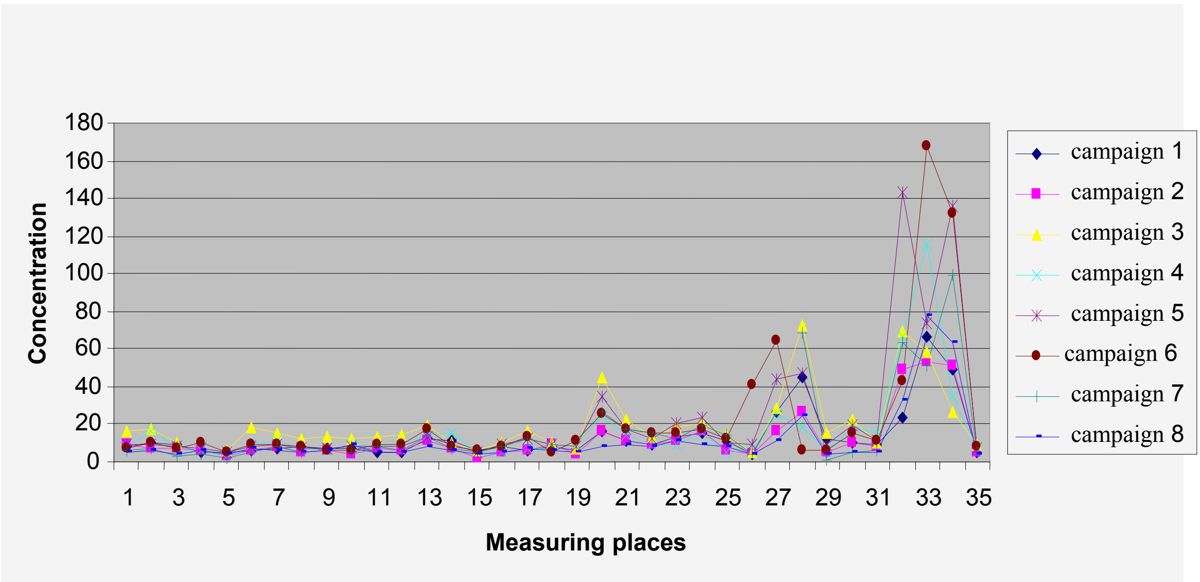


Fig. 9. Graphic presentation of toluene.

## DISCUSSION

Based on the presented results, it can be concluded that the greatest values of organic pollutants (benzene, xylene and toluene, as well as the total hydrocarbons) have been measured in the Industrial zone, more precisely Oil plant, in all the campaigns. The second biggest result in terms of the organic pollutants measured is outlet Oil plant into the channel which is in the vicinity of Petrochemical plant waste water and Fertilizer plant. We are concluding that the highest concentration of all the organic pollutants has been measured in effect zone Oil plant and at the outlet into the channel located between Fertilizer plant and Petrochemical plant.

The biggest measured values for inorganic industrial pollutants ($SO_2$, $NH_3$, $O_3$, NOx and $NO_2$) are in all the campaigns in effect zone Fertilizer plant ammonia, all nitrogen oxides, and sulphur dioxide is the highest in all the industry effect zones.

The effect of season on the measured values had been considered and it was concluded that the highest values of the measured organic pollutants (benzene) were in January (winter). The highest measured values for ammonia are in August (summer).

## CONCLUSION

Based on the analysis of the measurings by passive sampling method, it can be concluded that the increased concentrations of benzene-toluene-xylene in both measuring campaigns can be found in effect zone Oil plant, which leads to the conclusion that zone Oil plant is the highest source of pollution and that at the analysed places adequate technical-technological steps should be taken so that pollution could be significantly reduced.

The highest concentration of inorganic pollutant ammonia has been measured in effect zone Fertilizer plant, but the other nitrogen oxides have been measured in all industry and town effect zones. In all industry and town effect zones, other inorganic pollutants $SO_2$, $O_3$ have been measured.

Technical-technological measures for reducing organic and inorganic pollutants have been specified in industry action plans. After analysing emitters, *i.e.* the places generating organic and inorganic pollutants, activity plan is prepared specifying reconstruction of the tanks and pump stations, covering the facilities emitting the greatest quantities of organic and inorganic pollutants and in some cases introduction of a new technology that reduces emission, *i.e.* pollution.

Monitoring of organic and inorganic pollutants presents an important preventive measure providing important information for detecting the places that are at greatest risk. Consequently, in accordance with that, action plan can be prepared and adequate technical-technological measures envisaged, all for the purpose of integral control and pollution reduction.

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