

## Introduction of cleaner production in the tank farm of the Pancevo Oil Refinery, Serbia

Jovan Jovanovic<sup>a</sup>, Mica Jovanovic<sup>a,\*</sup>, Ana Jovanovic<sup>a</sup>, Vedrana Marinovic<sup>b</sup>

<sup>a</sup> University of Belgrade, Faculty of Technology and Metallurgy, Karnegijeva 4, 11120 Belgrade, Serbia

<sup>b</sup> Institute of Technical Sciences of the Serbian Academy of Science and Arts, Knez Mihajlova 35, 11120 Belgrade, Serbia

### ARTICLE INFO

#### Article history:

Received 23 January 2009

Received in revised form

4 January 2010

Accepted 4 January 2010

Available online 13 January 2010

#### Keywords:

TANKS emission models

Refinery tank farm

Minimization of VOC emissions

### ABSTRACT

This work studies the introduction of cleaner production (CP) in the tank farm of the Pancevo Oil Refinery. From 2003 to 2008, substantial investments in storage technology and equipment were made in order to minimize the emissions of volatile organic compounds (VOCs). This article analyzes the effects of the CP activities using a model of tank farm emissions before and after reconstruction. US EPA TANKS software was used in order to develop a comprehensive model of the tank farm emissions. The year 2006 was accepted as representative for the analyses and related technical and production data as well as meteorological information were employed in the development of the model. The results show that the total VOC emissions were 37.6% lower after reconstruction and that the emissions of the major pollutant benzene were decreased by 62.7%. The effects of the CP activities were analyzed through the reduction of ecological damage, elements related to the operating costs, liability issues and the company's image. Future tank farm reconstruction activities in the Oil Refinery, Pancevo were proposed and their environmental effects predicted. An indicator of the expected decrease in VOC pollution was developed and quantified, with the aim of its use for quick calculations in similar cases.

© 2010 Elsevier Ltd. All rights reserved.

### 1. Introduction

Oil refineries are large industrial plants in which crude oil is converted (refined) to petroleum products. The oil and gas refinery industry in Europe provides 42% of the energy requirements and 95% of the fuels required for transport by the operation of more than 100 refineries that process 700 million tones of crude oil per annum (EC, 2003). Each of these oil refineries is an emission source of various pollutants, mainly volatile organic compounds (VOCs), which have been the subject of various environmental analyses (Bevilacqua and Braglia, 2002; Abdul-Wahab et al., 2002; Cetin et al., 2003; Whitcombe et al., 2003; Mata et al., 2005; Ras et al., 2009; Tompa et al., 2005; Majumdar et al., 2008; Gielen et al., 2002; Ostermark, 1996; Khan and Ghoshal, 2000; Na et al., 2001; Liu et al., 2008; Amaral et al., 1996; Lin et al., 2004; Guo et al., 2007; Cheng et al., 2008; Clements and Cheng, 1982; Snider and Manning, 1982).

Oil, gas and petrochemical companies have always been the major environmental concern of the civil society. Huge multinational companies, such as Exxon Mobil, Royal Dutch Shell, BP and Chevron, have substantially changed their environmental policies by designing less polluting and safer processes and plants.

Numerous “end of pipe” and cleaner production technologies were developed and implemented aimed at reducing ecological damage and improving the companies' images. Nevertheless, the public often raise doubts and ask serious questions concerning the accuracy and the completeness of reports from the oil industry (Environmental Integrity Project, 2009). Refinery capacities have moved towards developing countries and the “new seven sisters” (Saudi Aramco – Saudi Arabia, JSC Gazprom – Russia, CNPC – China, NIOC – Iran, PDVSA – Venezuela, Petrobras – Brazil and Petronas – Malaysia) have emerged and taken the leading positions in the world's oil and gas industry. It is crucial that the new world leaders in crude oil processing clearly and quickly implement the best available CP techniques and new approaches in their operations (Silva and Amaral, 2009; Dovi et al., 2009; Karavanas et al., 2009; Fernandez and Ruiz, 2009; Klemes and Huisingh, 2008; Hojer et al., 2008; Ekins et al., 2007).

The location of each oil refinery experiences different degrees and forms of pollution. Therefore, a universal cleaner production philosophy and framework applies its principals through different approaches, for example like the one in the Baku Oil Refinery Factory JSC, Azerbaijan, with a joint cleaner production and energy efficiency program (The Government of Azerbaijan, 2009). The application in China of a fully regulated mandatory cleaner production approach, based on a cleaner production promotion law, incorporates a special regulation – a cleaner production

\* Corresponding author. Tel.: +381 11 3303 699; fax: +381 11 3370 387.

E-mail address: [mica@tmf.bg.ac.rs](mailto:mica@tmf.bg.ac.rs) (M. Jovanovic).

standard for the petroleum refinery industry (Cleaner Production in China, 2009; Ministry of Environmental Protection The People's Republic of China, 2009). The Mexican PEMEX has launched programs for cleaner production and efficient use of water in all of its operating subsidiaries, thereby reducing related costs. CO<sub>2</sub> emissions were reduced by 3.1 million t/y, i.e., by about 8% of the estimated 40 million t/y of emissions in 2001 (USAID, 2009). The Caltex Refinery in Lytton, Brisbane, Australia has implemented substantial changes in solid waste management. The BP oil refinery at Kwinana, Australia has implemented a number of cleaner production measures and is particularly active in reducing water consumption, greenhouse gases, volatile organic compounds and other air emissions, and promoting energy efficiency and improvement of the protection of ground and coastal waters (North Carolina Division of Pollution Prevention and Environmental Assistance, 2009; Curtin University of Technology, 2009; Berkel, 2007).

The main oil refinery installations in Serbia, the NIS Petrol Oil Refinery Pancevo (since 2009 owned by JSC Gazprom), are located near the town Pancevo, 15 km northeast from Belgrade, the capital of Serbia. The citizens of Pancevo have always blamed the oil refinery for the bad quality of the ambient air in the town. In the last eight years, full public awareness of environmental problems has developed and the citizens of Pancevo, its municipality officials and the Government of Serbia have put the industry under constant pressure to eliminate industrial sources of pollution. There have been many air pollution incidents in Pancevo that were connected with the operations of industrial installations. In 2004, the Municipality of Pancevo had an automated system for the measurement of pollutants in the ambient air installed at several locations in urban areas. In last few years, there were several occasions when the citizens of Pancevo were alarmed by sirens to remain in doors due to the presence of a high level of BTEX hazardous air pollutants (HAPs, benzene, toluene, ethylbenzene and xylenes), especially benzene, in the ambient air: 20/07/2008 – 100 µg/m<sup>3</sup> benzene, 06/02/2007 – 153.4 µg/m<sup>3</sup>, 05/02/2007 – 160.5 µg/m<sup>3</sup> and 14/11/2006 – 125.88 µg/m<sup>3</sup> (Pancevo town, 2009). Responding to serious public reactions of the civil society and pressures from the government and local institutions, the Refinery Pancevo decided to perform reconstruction of its storage facilities in order to minimize related hazardous BTEX emissions.

The Pancevo Oil Refinery has made substantial changes and large investments in its storage technology and equipment in the last five years in order to resolve one of the major air pollution problems at its source by minimizing the emission of VOC from its tank farm. The described activity commenced as pollution prevention and evolved into a cleaner production project. In this article a case study aimed at analyzing the effects of the mentioned activity is presented. For this purpose, a comprehensive model of the VOC emissions from the refinery was developed. The aim of the present study was to employ the developed model to quantify achieved reductions of ecological damage, based on which the other cleaner production elements (operating costs, liability issues and improvements of the image of the company) were developed. The cleaner production results achieved in Pancevo could be of wider interest for oil refineries, petrochemical plants and similar industrial facilities.

## 2. Case study elements

The NIS Petrol Oil Refinery Pancevo with a capacity of 4.8 million tones of crude oil prefabrication per annum is one of the largest factories in Serbia and the dominant supplier of the domestic and regional fuel market. The refinery produces different types of gasoline, diesel fuel, paraffin and aromatic solvents, raw materials for petrochemicals, bitumen, sulfur, liquefied petroleum gas, etc. The refinery handling department consists of loading and unloading

facilities and large tank farm in which crude oil, oil derivatives and refinery products are stored. The tank farm has 141 tanks, which cover around 2/3 of the surface of the refinery complex.

The major emission sources of air pollutants are the tanks used for storage of derivatives which contain VOCs, such as motor gasoline, solvents and intermediates. Some 40 tanks were the subject of activities aimed at minimizing emissions. The other tanks in the refinery are used for the storage of crude oil, diesel and fuel oil; therefore, the content of VOC in these liquids is significantly lower. The perception that the mentioned group of 40 storage tanks was one of the major emission sources to the ambient air in Pancevo was one of the key reasons for the decision to invest in the reconstruction. The second reason was the fact that in the previous decade the tank farm was poorly maintained, resulting in higher than normal VOC emissions. On the floating roof of the tanks, ring holes had formed due to insulation deterioration and large surfaces of the VOC in storage were exposed to the ambient air, enabling large emissions.

It should be documented that the reconstruction was mostly based on equipment recommendations and the best available technique guidelines (EC, 2003; European Commission, 2003) and was not supported by a detailed emission estimation analysis. The basic concept was to retrofit the external floating roof or to convert fixed roof tanks to domed external floating roof tanks. Reconstruction of the tanks commenced in 2004 and lasted until mid 2008, with the majority of the 27 tanks planned for reconstruction finished by mid 2006. The total investment for the refinery tank reconstruction was cc 40 million US\$. These 27 tanks are employed for the storage of various refinery derivatives: merox, raffinate, pyrolytical gasoline, light gasoline, special gasoline, stabilized gasoline, benzene, toluene, unleaded motor gasoline, motor gasoline, naphtha and alkylate.

Merox gasoline is obtained by the MEROX (mercaptan oxidation) process. This gasoline has a low octane number and is used for the blending of motor gasoline. Raffinate is a product of aromatic extraction and has a low octane number. It can be used in the gasoline blending unit and for the production of special gasolines. Pyrolytical gasoline is a by-product of naphtha pyrolysis in the Petrochemical complex and is transported by pipeline from this factory into the Oil Refinery. It has high amounts of aromatic compounds, a high density, low vapor pressure and a high octane number. Light gasoline is the primary component for gasoline blending and is a product of the crude distillation unit. It has a moderately high octane number. Stabilized gasoline has a higher octane number and a higher vapor pressure than light gasoline. It is used for motor gasoline blending. Naphtha is a product of the crude distillation unit. Alkylate (light and heavy) is the main product of the alkylation process. It has a high octane number (due to the presence of *iso*-paraffins) and is mostly used for the blending of unleaded motor gasoline. It has a low content of aromatic compounds. The mentioned derivatives have quite similar, or the same, compositions in different oil refineries. Therefore, the major characteristics of the Pancevo oil refinery derivatives that are being kept in its tank farm are presented in Table 1.

## 3. Modeling of VOC emissions

US EPA software "TANKS" was used in order to develop a comprehensive model of the tank farm emissions. TANKS (Emissions Estimation Software Version 4.09D) is a Windows-based computer software program that calculates VOC and HAP emissions from organic liquid storage tanks based on the emission estimation procedures developed in USA EPA's Compilation of Air Pollutant Emission Factors. The program is able to calculate air pollutant emissions by retrieving chemical properties from a software database of over 100 organic liquids. The program is based on storage equations and balances that were derived for petroleum

**Table 1**  
Characteristics of the refinery derivatives (average values).

No.	Storage liquid	Characteristics <sup>a</sup>
1.	Mercox	Density (15 °C) 0.675 g/cm <sup>3</sup> , 60%P, 15%A, 20%N <sup>a</sup>
2.	Raffinate	Density (15 °C) 0.745 g/cm <sup>3</sup> , 29%P, 30%A, 11%N
3.	Pyrolytical gasoline	Density (15 °C) 0.841 g/cm <sup>3</sup> , 25%P, 56%A, 10%N
4.	Light gasoline and stabilized gasoline	Density (15 °C) 0.641 g/cm <sup>3</sup> , 87%P, 3.4%A, 0.5%O
5.	Special gasoline	Density (15 °C) 0.714 g/cm <sup>3</sup> , 0.90%A
6.	Benzene	Density (15 °C) 0.878 g/cm <sup>3</sup> , 100%A
7.	Toluene	Density (15 °C) 0.871 g/cm <sup>3</sup> , 100%A
8.	Unleaded gasoline	Density (15 °C) 0.754 g/cm <sup>3</sup> , 40%P, 27%A, 12%N
9.	Leaded gasoline	Density (15 °C) 0.742 g/cm <sup>3</sup> , 50%P, 35%A, 12%N
10.	Naphtha	Density (15 °C) 0.718 g/cm <sup>3</sup> , 60%P, 12%A, 25%N
11.	Alkylate	Density (15 °C) 0.700 g/cm <sup>3</sup> , 56%P, 12%A, 18%N

<sup>a</sup> P – paraffins, A – aromatics, N – naphthenes, O – olefins.

products, such as gasoline, diesel fuel, jet fuel, stable crude, etc. TANKS is capable of calculating emissions of an individual component from known mixtures and of estimating emissions from crude oils and selected refined petroleum products using liquid concentration HAP profiles supplied with the program. The addition of more chemicals, if desired, is allowed. In the calculations, the software employs emission factors, representative values that attempt to relate the quantity of a pollutant released into the atmosphere with an activity associated with the release of that pollutant. These factors are usually expressed as the weight of pollutant divided by a unit weight, volume, distance, or duration of the activity emitting the pollutant. Application of factors facilitates software calculations for an estimation of emissions from various sources of air pollution. In the program embedded emission factors are averages of all available data of acceptable quality (US Environmental Protection Agency, 2009a,b; Jackson, 2006).

TANKS uses chemical, meteorological, as well as roof fitting and rim seal data to generate estimations of emissions from several types of storage tanks. The program allows the usage of its own meteorological database (of over 240 cities in the United States) or an installed new database of the location for which the emissions are to be calculated. A specific model was developed for the tank farm of the Oil Refinery Pancevo, Serbia using adequate data input, as follows:

1. individual tank specifications for 27 tanks,
2. detailed characteristics of the oil derivatives,
3. meteorological data of the Pancevo location (temperature, wind, solar flux etc.), and
4. data related to the operation of a tank.

The required data regarding the tank characteristics were collected in the Oil Refinery Pancevo. Detailed characteristics of the oil derivatives (representative amounts of the components in the petroleum mixtures of the refinery) were obtained based on laboratory reports from the refinery's ISO 17025 accredited laboratory (Association of Accredited Laboratories, Serbia, 2009). With these data, TANKS is able to relate chemical properties from its database with the representative content of each petroleum mixture stored in each of the tanks in the refinery's tank farm.

Meteorological data were obtained from annual reports of the Republic Hydrometeorological Service of Serbia for the area of Pancevo (Republic Hydrometeorological Service of Serbia, 2009). The parameter solar radiation (solar radiation energy received on a given surface area in certain period, (World Meteorological Organization, 2008)) is embedded in the model using average monthly values. The data embedded in the tank models related to the ambient air temperature of Pancevo are illustrated in Fig. 1.

Derivatives' characteristics and meteorological data should be regarded as stable. Related average values of derivatives characteristics

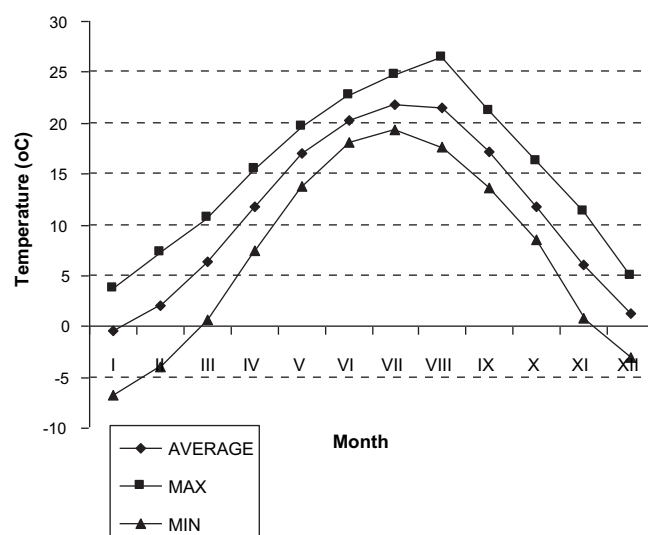


Fig. 1. Ambient air temperature profile for Pancevo, Serbia.

are presented in Table 1. Meteorological data does not change significantly in time. Data related to tank operation (listed as 4.), especially the average fluid flow, sequences in which the tanks are being loaded and unloaded, the period of the year in which the tanks do or do not have intense operation, etc. are those that vary annually and are related to the various production elements of the Oil Refinery Pancevo. The year 2006 was accepted as the reference year for analyses because of its stable and high production level. A series of individual tank emission models were developed for the reference year. The consistency of data and its adequacy in the model were evaluated through series of sensitivity analyses which were performed with developed model (Jovanovic et al., 2008a,b). A monthly approach to the modeling of the tank emissions was employed (rather than a yearly one) in order to achieve more precise results. Therefore, each of the individual tank models developed for a year of operation represents the sum of 12 individual monthly models.

The emissions of each individual tank and stored liquid were calculated using the developed model. The model calculations were realized for each month separately and the obtained results are presented for the representative year in Tables 2 and 3.

VOC emissions from the floating roof tanks before their reconstruction were 143,300 kg/y, of which benzene emissions were 6181.5 kg/y. After reconstruction, the emissions from the domed floating roof tanks declined to 13,089 kg/y, of which benzene emissions are 731 kg/y. The remaining part of the tank farm, which consists of fixed roof tanks that were not changed during the CP reconstruction, produces 203,239 kg of emissions per year, of which 2503 kg/y are benzene emissions.

Taking into account the data from Table 2, which presents the results of the emissions before and after the reconstruction of 27 tanks (reductions from retrofit actions), and the results from Table 3, which presents the emissions from the non-reconstructed fixed roof part of the VOC tank farm, some summary statements related to the emissions of the tank farm before and after reconstruction can be presented as follow.

- VOC emissions from the Oil Refinery, Pancevo before the reconstruction were on the level of 346,539 kg/y (benzene emissions were 8685 kg/y or 2.51%);
- VOC emissions from Oil Refinery, Pancevo after the reconstruction are on the level of 216,328 kg/y (benzene emissions are 3235 kg/y or 1.50%);

**Table 2**  
Emissions from the Oil Refinery, Pancevo tanks before and after reconstruction.

No	Tank symbol/ capacity (m <sup>3</sup> )	Storage liquid	Before reconstruction			After reconstruction		
			Tank type	Total emission (kg/y)	Benzene emission (kg/y)	Tank type	Total emission (kg/y)	Benzene emission (kg/y)
1.	FB 0701 4500	Merox	External floating roof	4402.53	26.30	Domed external floating roof	522.85	3.73
2.	FB 0707 540	Raffinate	External floating roof	3337.22	9.81	Domed external floating roof	192.83	0.58
3.	FB 0708 540	Pyrolytical gasoline	External floating roof	4041.33	651.12	Domed external floating roof	275.29	275.29
4.	FB 0717 3800	Light gasoline and stabilized gasoline	External floating roof	12563.50	40.52	Domed external floating roof	1141.91	5.16
5.	FB 0718 3800	Light gasoline and stabilized gasoline	External floating roof	12563.50	40.52	Domed external floating roof	1141.91	5.16
6.	FB 1101 1000	Benzene	Fixed – roof	2143.81	2143.81	Domed external floating roof	103.53	103.53
7.	FB 1106 540	Benzene	Fixed – roof	838.75	838.75	Domed external floating roof	84.58	84.58
8.	FB 1107 540	Benzene	Fixed – roof	838.75	838.75	Domed external floating roof	84.58	84.58
9.	FB 1103 1000	Toluene	Fixed – roof	836.74	0.00	Domed external floating roof	36.19	0.00
10.	FB 1301 4510	Unleaded gasoline	External floating roof	5871.54	87.22	Domed external floating roof	557.89	9.65
11.	FB 1302 4510	Unleaded gasoline	External floating roof	5871.54	87.22	Domed external floating roof	557.89	9.65
12.	FB 1311 1000	Unleaded gasoline	External floating roof	5136.91	75.70	Domed external floating roof	361.51	5.98
13.	FB 1312 1000	Unleaded gasoline	External floating roof	5136.91	75.70	Domed external floating roof	361.51	5.98
14.	FB 1313 1000	Unleaded gasoline	External floating roof	5136.91	75.70	Domed external floating roof	361.51	5.98
15.	FB 1314 1000	Unleaded gasoline	External floating roof	5136.91	75.70	Domed external floating roof	361.51	5.98
16.	FB 1306 4510	Leaded gasoline	External floating roof	5852.33	120.21	Domed external floating roof	573.42	14.08
17.	FB 1308 4510	Leaded gasoline	External floating roof	5852.33	120.21	Domed external floating roof	573.42	14.08
18.	FB 1309 10150	Leaded gasoline	External floating roof	6608.37	133.33	Domed external floating roof	675.75	14.08
19.	FB 1310 10150	Leaded gasoline	External floating roof	6608.37	133.33	Domed external floating roof	675.75	14.08
20.	FB 1315 1000	Leaded gasoline	External floating roof	5153.95	105.13	Domed external floating roof	378.45	9.11
21.	FB 1316 1000	Leaded gasoline	External floating roof	5153.95	105.13	Domed external floating roof	378.45	9.11
22.	FB 1405 21700	Leaded gasoline	External floating roof	7883.59	160.01	Domed external floating roof	969.12	21.02
23.	FB 1406 21700	Leaded gasoline	External floating roof	7883.59	160.01	Domed external floating roof	969.12	21.02
24.	FB 1903 13000	Naphtha	External floating roof	4865.72	38.66	Domed external floating roof	532.70	4.45
25.	FB 1904 13000	Naphtha	External floating roof	4865.72	38.66	Domed external floating roof	532.70	4.45
26.	FB 2007 1100	Alkylate	External floating roof	4357.63	0.00	Domed external floating roof	342.22	0.00
27.	FB 2008 1100	Alkylate	External floating roof	4357.63	0.00	Domed external floating roof	342.22	0.00
Total				143,300	6181.5		13088.81	731.31

- The present major individual contribution to VOC emissions are produced by the operations in two stabilized gasoline fixed roof tanks with 167,293 kg VOC emissions per year (benzene emissions 347.4 kg/y), and by the benzene fixed roof tank with 2144 kg of benzene emissions per year. Benzene emissions from these three tanks represent 77% of the total benzene emissions from the tank farm.

It should be noted that VOCs tank farm emission model of the Oil Refinery Pancevo was developed after the retrofit investment decisions have been made and served as a tool for transformation of pollution prevention into cleaner production activity.

The developed model and the obtained results formed the base for the calculation of an informative air pollution reduction indicator for quick calculations of the emissions reductions (*I*) that could be expected by the large scale reconstruction of external floating roof and fixed – roof tanks into domed external floating roof tanks in oil refineries (in our case 27 tanks have been reconstructed). For this purpose air pollution reduction indicator is defined as a relation between achieved VOCs emission reduction by reconstruction from existing (external floating roof and fixed – roof tanks with VOCs emission  $E_0$ ) into domed external floating roof tanks (VOCs emission  $E_{DEFT}$ ), and the emission before the reconstruction. Its mathematical expression and illustrative calculation based on the cumulative data from Table 2 is presented as follows:

$$I = (E_0 - E_{DEFT})/E_0$$

$$= (143,300 - 13088.81)[\text{kg/y}]/143,300[\text{kg/y}] = 0.90866$$

Indicator value for the case of Oil Refinery, Pancevo was *cc a* 91%. Calculated value could be taken into consideration in refineries

with similar problems, meaning that they could expect an approximately 10-fold improvement by the tank reconstruction from existing into domed external floating roof tanks.

#### 4. Cleaner production effects

In order to define the effects of the described cleaner production activities, it was necessary to analyze the achieved reductions in ecological damage, as well as different elements related to the operating costs, liability issues and the company's image.

Comparison in total VOC and benzene emissions before and after the reconstruction is displayed in Fig. 2. The main benefits of

**Table 3**  
Emissions from the Oil Refinery, Pancevo fixed roof tanks.

No	Tank symbol/ capacity (m <sup>3</sup> )	Storage liquid	Tank type	Total emission (kg/y)	Benzene emission (kg/y)
1.	FB 0710 540	Raffinate	Fixed – roof	2642.87	7.94
2.	FB 0805 2530	Special gasoline	Fixed – roof	11265.04	1.56
3.	FB 0806 2530	Special gasoline	Fixed – roof	11265.04	1.56
4.	FB 1108 450	Special gasoline	Fixed – roof	2386.36	0.33
5.	FB 1109 450	Special gasoline	Fixed – roof	2386.36	0.33
6.	FB 1110 143	Special gasoline	Fixed – roof	755.06	0.10
7.	FB 1111 143	Special gasoline	Fixed – roof	755.06	0.10
8.	FB 1112 143	Special gasoline	Fixed – roof	755.06	0.10
9.	FB 1113 143	Special gasoline	Fixed – roof	755.06	0.10
10.	FB 0807 1420	Stabilized gasoline	Fixed – roof	83646.40	173.70
11.	FB 0808 1420	Stabilized gasoline	Fixed – roof	83646.40	173.70
12.	FB 1102 1000	Benzene	Fixed – roof	2143.81	2143.81
13.	FB 1104 1000	Toluene	Fixed – roof	836.74	0.00
Total				203239.30	2503.33

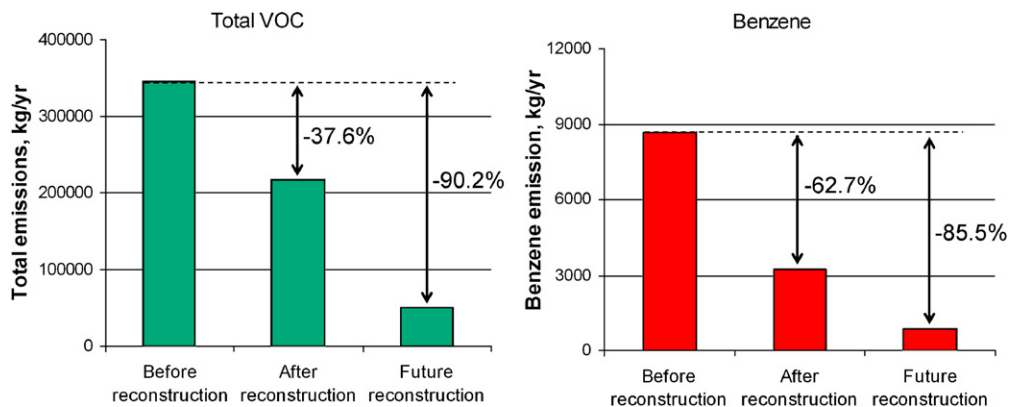


Fig. 2. Total VOC and benzene emissions before, after and with future reconstruction.

the CP activities in the Oil refinery, Pancevo are the following emission reductions.

- VOC emissions from the Oil Refinery, Pancevo have decreased by cc 37.6%.
- Benzene emissions have decreased by cc a 62.7%.
- Emissions in the reconstructed part of the refinery’s tank farm have decreased by cc a 91%.

It should be noted that the level of emissions pollution before the reconstruction of the tank farm was higher than the data obtained from the model because of the poor maintenance of the external floating roof tanks, which caused the formation of large holes in the rim insulation, allowing direct contact of the surfaces of the derivatives with the ambient air.

Serbian environmental regulations define limits for (i) aromatic hydrocarbon emissions from stored oil products of 8 mg/m<sup>3</sup> for the total VOCs and (ii) concentrations in the ambient air as follows: max. 10 µg/m<sup>3</sup> for benzene (year 2006) and 7.5 µg/m<sup>3</sup> for toluene. The benzene limit must be lowered to the level of 5 µg/m<sup>3</sup> by the year 2015, each year by 0.5 µg/m<sup>3</sup> commencing from 2006 (the benzene limit for 2009 is 8.0 µg/m<sup>3</sup>) (Official Gazette of the Republic of Serbia, 1997, 1992). It should be noted that the limit concentrations in the ambient air are much stricter than the twelve-year-old emission limits; therefore the environmental regulations are generating adequate pressure.

The lower emissions from the reconstructed tank farm have reduced ecological damage to the environment. The results of the measurement of the key contaminant benzene in the ambient air at the location Vojlovica, some 3 km from the Oil Refinery, Pancevo in the direction of the major south-east wind stream, are presented in Fig. 3. The average monthly concentrations of benzene in 2006 (average year 6.70 µg/m<sup>3</sup>, 2007 (3.73 µg/m<sup>3</sup>) and the first five months of 2008 (4.00 µg/m<sup>3</sup>) are significantly lower than in 2005 (9.61 µg/m<sup>3</sup>) (Pancevo town, 2009). The reduction in average annual ambient air concentrations of benzene after the reconstruction of the tank farm is clearly visible from environmental data presented in Fig. 4. It is important to point out that, in that period, the reconstruction of the refinery tank farm was the only major environment-related activity in the Oil refinery, Pancevo and in the industrial zone as well. The measured benzene concentrations are influenced by other emissions from the oil refinery, emissions from activities in the nearby petrochemical complex and road traffic. The work on the tank farm reconstruction started in 2006 and was finished in 2007. Fig. 4 shows that significant reduction in average annual ambient air benzene concentrations is achieved during (30.2% reduction, 2006 vs. 2005) and after the reconstruction (62.7% reduction, 2007 and 2008 vs. 2005). Furthermore, average annual ambient air benzene concentrations remain relatively constant after the reconstruction. Considering that the refinery tank reconstruction was the only major environmental activity performed in that period, while the other polluting factors

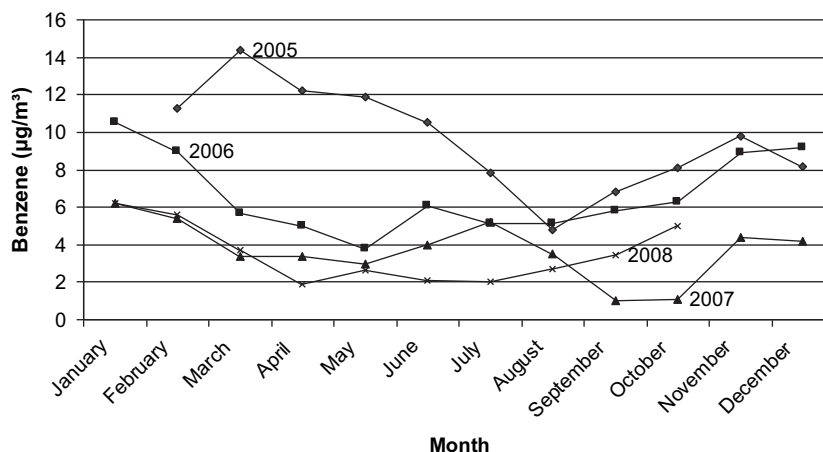


Fig. 3. Benzene in the ambient air near the Oil Refinery, Pancevo.

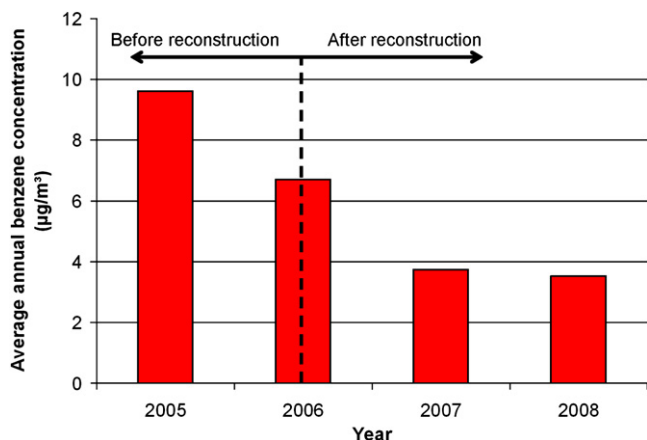


Fig. 4. Reduction in average annual ambient air benzene concentrations after the tank farm reconstruction.

remained unchanged, the presented data indicates that lower VOC emissions from refinery tank farm have had positive effects on the quality of the ambient air, reducing the average annual ambient air benzene concentrations by 62.7%.

The tank farm reconstruction was a rather high investment of Oil refinery Pancevo (cc 40 million \$US). The volume of compounds which are now not lost through emissions (hundreds of t/y) compared with the huge refinery output (cc 600,000 t/y) is very small. Their value and share in the refinery's material costs could be neglected. Total costs of environmental protection are much higher than executives usually think having in mind the costs of material, energy and labour. Therefore, the costs analyses should focus on other related elements, among which the most important are the production shutdown costs (Hamner, 2009).

The Serbian Ministry in charge of the environment has introduced the practice to order the immediate stop of all production activities in the Oil Refinery whenever the benzene concentration in the ambient air of Pancevo reaches a value over  $100 \mu\text{g}/\text{m}^3$ . The operating costs of each refinery shut down/start up is on the level of millions of \$US, not to mention the huge organizational and technical problems and related costs. The absolute priority of the Refinery is, therefore, to avoid such situations.

Analyses related to the measurement of Pancevo tank farm investment efficiency have defined three levels of refinery's shutdown costs, as follows: (a) full refinery shutdown/start up/lost income costs – cc a 2 million \$ US, (b) partial shutdown/start up/lost income – cc a 1 million \$ US, (c) isolated disturbance/shutdown/lost income in production – cc a 0.5 million \$ US. If the investment in tank farm was not performed authorities orders to shut up refinery's production would probably have had scenario as follows: 1 full refinery shutdown per year with a cost of 2 million \$ US, 4 partial refinery shutdown per year with a cost of 4 million \$ US and 8 individual plants shutdown per year with a cost of 4 million \$ US. Total estimation of shutdown/start up/costs and lost income is 10 million \$ US per year. Refinery's management would probably be able to predict those situations and couple it with regular maintenance activities in order to decrease costs in some 20% cases. Final estimation of related costs is 8 million \$ US per year. Return on investment calculation of tank farm reconstruction based on presented data is 5 years.

The new Serbian environmental regulation, which has been in force since 2008, has given the Serbian Environmental Protection Agency the authority to control industrial emissions, aiming at the full implementation of the "polluter pays" principle. An environmental registry (cadastre) fully in line with the PRTR protocol of the

Aarhus Convention and relevant EU regulation has been introduced, whereby industrial producers must report their measured or calculated emissions (Hamner, 2009; Official Gazette of the Republic of Serbia, 2007; United Nations Economic Commission for Europe, 2009; European Parliament and Council, 2006). The Oil Refinery Pancevo has the obligation to report on 18 different air-contaminating substances, among which are VOCs. Verified reports are the base for related environmental tax costs calculations (inadequate or incorrect reports, with lower than real emissions, are to be seriously fined). For each of its activities that cause environmental damage, the Oil Refinery, Pancevo has to pay related environmental operating cost. The intention of the Serbian government is to constantly increase environmental costs related to pollution (detailed cost data are not available at the moment because it is the first year of the implementation of the regulation). The presented information, together with the data shown in Fig. 2, indicates that lower VOC emissions from refinery tank would exclude the possibility of environmental refinery production shut down and the thereby generated huge operational costs. Accurate elaboration of environmental registry reports based on the tank farm emission model will produce reliable data for related environmental tax costs calculations, with the aim of decreasing both emissions and costs.

The Environmental Law and the Criminal Law of Serbia both define high sanctions for producers that fail to implement environmental measures and release polluting substances (Official Gazette of the Republic of Serbia, 2004, 2005). In the last five years, a dozen environmental and criminal law processes have commenced against the refinery and its managers, of which most are still in the court of law (with very few convictions due to the long procedures). The primary indictment of these processes is ecological damage to the ambient air by pollutant emissions, primarily benzene. The lower VOC emissions from the refinery tank farm are good news, which should be utilized for improving the very bad image of the Oil Refinery Pancevo Company. The presentation of valid technical data of lower emissions calculated using the developed model, the decrease in the environmental tax costs, the decrease in the environmental inspection orders, the decrease in the refinery's liability law cases, etc. would produce an ambient for positive public reactions and, in time, improve the damaged image of the company.

## 5. Future activities

The VOCs emissions data from each of the tanks in Oil Refinery Pancevo were not available and taken into account before retrofit reconstruction and some substantial VOCs emitters were left unchanged. Therefore, future activities in the refinery tank farm should focus on the remaining 13 tanks with very high VOC emissions of some 203 t/y, of which emissions of benzene are 2.5 t/y (Table 3). The priority should be the minimization of the carcinogenic benzene emissions.

Proposal for future tank farm reconstruction activities is presented in Table 4. The benzene storage tank FB 1102, with 85.6% of the total calculated emissions, should be reconstructed first, as soon as possible. The model predicts that its reconstruction from a fixed roof to a domed external floating roof tank should result in significantly lower benzene emissions: from 2144 kg/y to 103 kg/y. The second priority should be a similar reconstruction of the tanks for stabilized gasoline FB 0807/8, aimed at lowering the high VOC emissions from 167293 kg/y to 3435 kg/y.

If the model had been developed before the retrofit investment, related decisions would have been different. Comparison of data presented in Tables 2 and 4 shows that not reconstructed tanks FB 1102 and FB 0807/8 have VOCs emission, particularly benzene, bigger than some of the reconstructed tanks.

**Table 4**

A future reconstruction proposal with emissions reductions.

No	Tank symbol / capacity (m <sup>3</sup> )	Storage liquid	Before reconstruction			After reconstruction		
			Tank type	Total emission (kg/y)	Benzene emission (kg/y)	Tank type	Total emission (kg/y)	Benzene emission (kg/y)
1.	FB 0710/540	Raffinate	Fixed – roof	2642.87	7.94	Domed external floating roof	132.14	0.26
2.	FB 0805/2530	Special gasoline	Fixed – roof	11265.04	1.56	Domed external floating roof	563.25	1.13
3.	FB 0805/2530	Special gasoline	Fixed – roof	11265.04	1.56	Domed external floating roof	563.25	1.13
4.	FB 0807/1420 <sup>a</sup>	Stabilized gasoline	Fixed – roof	83646.40	173.70	Domed external floating roof	1717.35	3.83
5.	FB 0808/1420 <sup>a</sup>	Stabilized gasoline	Fixed – roof	83646.40	173.70	Domed external floating roof	1717.35	3.83
6.	FB 1102/1000 <sup>a</sup>	Benzene	Fixed – roof	2143.81	2143.81	Domed external floating roof	103.53	103.53

<sup>a</sup> Proposed for future reconstruction.

The reduction of total VOC and benzene emissions for the proposed future reconstruction is shown in Fig. 2. If the proposed reconstruction of these three tanks is realized, VOC emissions from the Oil Refinery, Pancevo could decrease from today's level of 216,328 kg/y to 50,429 kg/y (a 76.7% decrease from 2006) and benzene emissions from 3235 kg/y to 854 kg/y (a 73.6% decrease from 2006). This would represent the overall reduction in total VOC and benzene emissions before the initial reconstruction of 90.2% and 85.5%, respectively (Fig. 2).

## 6. Conclusions

The introduction of cleaner production in the tank farm of the Pancevo Oil Refinery was expensive but an environmentally justifiable decision. The tank farm after reconstruction showed a significant decrease in the level of VOC emissions. The main concept of the reconstruction was to retrofit external floating roof tanks with a domed internal floating roof or to add an internal floating roof onto fixed roof tanks. An analysis of the emission reduction was performed by comparing estimations of the losses from the tank farm before and after reconstruction, based on the specific tank farm VOC emission model developed using US EPA TANKS software. The total emissions were lowered by 37.6% and that of the major carcinogenic pollutant benzene were lowered by 62.7%. There is an indication of a decrease in the ecological damage in the Pancevo environment. The lower benzene emissions resulted in a significant decrease of its concentration in the nearby ambient air, as registered by the Vojlovica monitoring station, from 9.61 µg/m<sup>3</sup> to 4.00 µg/m<sup>3</sup>, or a 58% decrease. The CP activities in the tank farm should continue, focusing on benzene emissions, with the reconstruction of three more fixed roof tanks into domed floating roof tanks. The future reconstruction, as proposed in this article, should produce a further significant decrease in benzene emissions of 85.5%.

An indicator for quick calculations of related CP contributions to the decrease in air pollution resulting from the reconstruction of external floating roof oil refinery tanks into domed external floating roof tanks was developed based on the data from the developed model. Its value is a 91% decrease in emissions, or approximately a 10-fold improvement.

VOC emissions from the oil refinery tank farm were significantly lowered by the reconstruction, however not completely eliminated. Emissions from refinery tanks cannot be measured but they can, and should be put under precise and adequate control by the development of tank farm emissions models. Once developed, these models could be used for the determination of possible emission reductions, recalculation of emissions for different actual technical data and meteorological conditions, as well as for the development of obligatory environmental reports and the calculation of related environmental state taxes. The reported case study of the Oil Refinery, Pancevo showed that the development of emissions models based on TANKS is an adequate tool to support CP

investment decisions. If such an approach had been used in the past, which was not the case in the presented study, better results between effects and investment costs could have been achieved and future reconstruction might not be necessary.

## Acknowledgments

The authors are grateful to the NIS Petrol, Serbia and the Ministry of Science and Technological Development of the Republic of Serbia for the support (project TR 21006).

## References

- Abdul-Wahab, S.A., Al-Alawi, S.M., El-Zawahry, A., 2002. Patterns of SO<sub>2</sub> emissions: a refinery case study. *Environmental Modelling and Software* 17, 563–570.
- Association of Accredited Laboratories, Serbia. Pancevo Oil Refinery Laboratory. [www.lab.org.rs/rmp.html](http://www.lab.org.rs/rmp.html) (accessed 06.09.09).
- Amaral, O.C., Otero, R., Grimalt, J.O., Albaiges, J., 1996. Volatile and semi-volatile organochlorine compounds in tap and riverine waters in the area of influence of a chlorinated organic solvent factory. *Water Research* 8, 1876–1884.
- Berkel, R., 2007. Cleaner production and eco-efficiency initiatives in Western Australia 1996–2004. *Journal of Cleaner Production* 8–9, 741–755.
- Bevilacqua, M., Braglia, M., 2002. Environmental efficiency analysis for ENI oil refineries. *Journal of Cleaner Production* 10, 85–92.
- Cetin, E., Odabasi, M., Seyfioglu, R., 2003. Ambient volatile organic compound (VOC) concentrations around a petrochemical complex and a petroleum refinery. *Science of the Total Environment* 312, 103–112.
- Cheng, W.H., Hsu, S.K., Chou, M.S., 2008. Volatile organic compound emissions from wastewater treatment plants in Taiwan: Legal regulations and costs of control. *Journal of Environmental Management* 4, 1485–1494.
- Clements, L.D., Cheng, S.W., 1982. Characterization of hydrocarbon pollutant burdens in petrochemical and refinery process streams. *Environment International* 4, 259–265.
- Cleaner Production in China. Cleaner Production Promotion Law. [www.chinacp.org.cn/eng/cppolicystrategy/cp\\_law2002.html](http://www.chinacp.org.cn/eng/cppolicystrategy/cp_law2002.html) (accessed 06.09.09).
- Curtin University of Technology. Cleaner Production at Curtin. [www.c4cs.curtin.edu.au/c4cs/c4csresearchchcrp3b1.htm](http://www.c4cs.curtin.edu.au/c4cs/c4csresearchchcrp3b1.htm) (accessed 06.09.09).
- Dovi, V.G., Friedler, F., Huisingh, D., Klemes, J., 2009. Cleaner energy for sustainable future. *Journal of Cleaner Production* 17, 889–895.
- EC, Integrated Pollution Prevention and Control (IPPC), Reference Document on the Best Available Techniques for Mineral Oil and Gas Refineries, February 2003.
- Environmental Integrity Project. Worst Oil Refineries Produce Significantly More Carcinogenic Air Pollution than Other Facilities, Raising Questions about Consistency of Oil Industry Reporting. [www.environmentalintegrity.org/pubs/020807%20TRI%20EIP%20news%20rews%20release%20FINAL%20\\_2\\_.pdf](http://www.environmentalintegrity.org/pubs/020807%20TRI%20EIP%20news%20rews%20release%20FINAL%20_2_.pdf) (accessed 06.09.09).
- Ekins, P., Vanner, R., Firebrace, J., 2007. Zero emissions of oil in water from offshore oil and gas installations: economic and environmental implications. *Journal of Cleaner Production* 15, 1302–1315.
- European Commission. Integrated Pollution Prevention and Control (IPPC): Reference Document on the Best Available Techniques in the Large Volume Organic Chemical Industry, February 2003.
- European Parliament and Council, 18/01/2006. Regulation (EC) No 166/2006 of the European Parliament and of the Council of 18 January 2006 concerning the establishment of a European Pollutant Release and Transfer Register. Official Journal of the European Union, 17, Strasbourg.
- Fernandez, I., Ruiz, M.C., 2009. Descriptive model and evaluation system to locate sustainable industrial areas. *Journal of Cleaner Production* 17, 87–100.
- Gielen, D.J., Moriguchi, Y., Yagita, H., 2002. CO<sub>2</sub> emission reduction for Japanese petrochemicals. *Journal of Cleaner Production* 10, 589–604.
- Guo, H., So, K.L., Simpson, I.J., Barletta, B., Meinardi, S., Blake, D.R., 2007. C<sub>1</sub>–C<sub>8</sub> volatile organic compounds in the atmosphere of Hong Kong: Overview of atmospheric processing and source apportionment. *Atmospheric Environment* 7, 1456–1472.

- Hamner, B. Management Accounting: The Hidden Driver for Clean Production. [www.cleanerproduction.com/Pubs/pubs/MgtAcctgandP2.html](http://www.cleanerproduction.com/Pubs/pubs/MgtAcctgandP2.html) (accessed 06.09.09).
- Hojer, M., Ahlroth, S., Dreborg, K.H., Ekvall, T., Finnveden, G., Hjelml, O., Hochschorner, E., Nilsson, M., Palm, V., 2008. Scenarios in selected tools for environmental systems analysis. *Journal of Cleaner Production* 16, 1958–1970.
- Jackson, M., 2006. Organic liquids storage tanks volatile organic compounds (VOCs) emissions, dispersion and risk assessment in developing countries: the case of Dar-Es-Salaam City, Tanzania. *Environmental Monitoring and Assessment* 116, 363–382.
- Jovanovic, A., Jovanovic, M., Petrovic, S., Babovic, N. Analysis of factors that influence hydrocarbon storage emission. In: IEEP 2008 Regional Conference Industrial Energy and Environmental Protection in Southeast Europe, June 2008.
- Jovanovic, A., Jovanovic, M., Petrovic, S., Babovic, N. Estimation of Benzene emission as a function of different storage. In: IEEP 2008 Regional Conference Industrial Energy and Environmental Protection in Southeast Europe, June 2008.
- Karavanas, A., Chaloulakou, A., Spyrellis, N., 2009. Evaluation of the implementation of best available techniques in IPPC context: an environmental performance indicators approach. *Journal of Cleaner Production* 17, 480–486.
- Khan, F.I., Ghoshal, A.K., 2000. Removal of volatile organic compounds from polluted air. *Journal of Loss Prevention in the Process Industries* 6, 527–545.
- Klernes, J., Huisingsh, D., 2008. Economic use of renewable resources, LCA, cleaner batch processes and minimising emissions and wastewater. *Journal of Cleaner Production* 16, 159–163.
- Lin, T.Y., Sree, U., Tseng, S.H., Chiu, K.H., Wu, C.H., Lo, J.G., 2004. Volatile organic compound concentrations in ambient air of Kaohsiung petroleum refinery in Taiwan. *Atmospheric Environment* 25, 4111–4122.
- Liu, P.W.G., Yao, Y.C., Tsai, J.H., Hsu, Y.C., Chang, L.P., Chang, K.H., 2008. Source impacts by volatile organic compounds in an industrial city of southern Taiwan. *Science of the Total Environment* 1–3, 154–163.
- Majumdar, D., Dutta, C., Mukherjee, A.K., Sen, S., 2008. Source apportionment of VOCs at the petrol pumps in Kolkata, India: exposure of workers and assessment of associated health risk. *Transportation Research Part D* 13, 524–530.
- Mata, T.M., Smith, R.L., Young, D.M., Costa, C.A.V., 2005. Environmental analysis of gasoline blending components through their life cycle. *Journal of Cleaner Production* 13, 512–523.
- Ministry of Environmental Protection The People's Republic of China. Environmental Regulations and Standards. [www.english.mep.gov.cn/standards\\_reports/standards/others1/Cleaner\\_Production\\_Standards/200710/t20071024\\_112039.htm](http://www.english.mep.gov.cn/standards_reports/standards/others1/Cleaner_Production_Standards/200710/t20071024_112039.htm) (accessed 30.06.09).
- Na, K., Kim, Y.P., Moon, K.C., Moon, I., Fung, K., 2001. Concentrations of volatile organic compounds in an industrial area of Korea. *Atmospheric Environment* 15, 2747–2756.
- North Carolina Division of Pollution Prevention and Environmental Assistance. Solid Waste Management at Caltex Refinery, Lytton, Qld. [www.p2pays.org/ref/04/03325.htm](http://www.p2pays.org/ref/04/03325.htm) (accessed 06.09.09).
- Ostermark, U., 1996. Better use of cleaner petrol. *Journal of Cleaner Production* 2, 105–110.
- Official Gazette of the Republic of Serbia No 54/92, 30/99 and 19/2006. The Ministry of Environment: By-law on limit values, methods of air quality metering, criteria for determination of measuring points and data recording. 16/08/92, Belgrade.
- Official Gazette of the Republic of Serbia No 30/97 and 35/97 The Ministry of Environment: By-law on emission limit values, measurement methods and terms and data recording. 23/07/97, Belgrade.
- Official Gazette of the Republic of Serbia No 135/04. National Assembly of the Republic of Serbia: Environmental Law of Serbia, 21/12/2004, 52 pp.
- Official Gazette of the Republic of Serbia No 85/05. National Assembly of the Republic of Serbia: Criminal Law of Serbia, 29/09/2005, 150 pp..
- Official Gazette of the Republic of Serbia No 94/2007. The Ministry of Environment: Regulation on the Methodology of Pollutants Registers Elaboration. 26/10/2007, Belgrade.
- Pancevo Town. Ecology: Monthly Reports. [www.ekologija.pancevo.rs/articles/details.aspx?id=592](http://www.ekologija.pancevo.rs/articles/details.aspx?id=592) (accessed 30.06.09).
- Ras, M.R., Marcé, R.M., Borrull, F., 2009. Characterization of ozone precursor volatile organic compounds in urban atmospheres and around the petrochemical industry in the Tarragona region. *Science of the Total Environment* 407, 4312–4319.
- Republic Hydrometeorological Service of Serbia. Climatology. [www.hidmet.gov.rs/latin/meteorologija/klimatologija\\_produkta.php](http://www.hidmet.gov.rs/latin/meteorologija/klimatologija_produkta.php) (accessed 06.09.09).
- Snider, E.H., Manning, F.S., 1982. A survey of pollutant emission levels in wastewaters and residuals from the petroleum refining industry. *Environment International* 4, 237–258.
- Silva, P.R.S., Amaral, G., 2009. An integrated methodology for environmental impacts and costs evaluation in industrial processes. *Journal of Cleaner Production* 17, 1339–1350.
- Tompa, A., Jakab, M.G., Major, R., 2005. Risk management among benzene-exposed oil refinery workers. *International Journal of Hygiene and Environmental Health* 208, 509–516.
- The Government of Azerbaijan. National Environmental Action Plan. [www.eco.aznet.org/01-09.html](http://www.eco.aznet.org/01-09.html) (accessed 06.09.09).
- USAID. Cleaner Production in Pemex, Mexico. [www.usembassy-mexico.gov/texts/et031003AIDPemex.html](http://www.usembassy-mexico.gov/texts/et031003AIDPemex.html) (accessed 06.09.09).
- US Environmental Protection Agency. Emission Factors. [www.epa.gov/ttn/chieff/ap42/index.html](http://www.epa.gov/ttn/chieff/ap42/index.html) (accessed 06.09.09).
- US Environmental Protection Agency. TANKS Emissions Estimation Software, Version 4.09D. [www.epa.gov/ttn/chieff/software/tanks/index.html](http://www.epa.gov/ttn/chieff/software/tanks/index.html) (accessed 14.11.09).
- United Nations Economic Commission for Europe. Aarhus Convention. [www.unecp.org/env/pp/prtr.htm](http://www.unecp.org/env/pp/prtr.htm) (accessed 06.09.09).
- Whitcombe, J.M., Cropp, R.A., Braddock, R.D., Agranovski, I.E., 2003. Application of sensitivity analysis to oil refinery emissions. *Reliability Engineering and System Safety* 79, 219–224.
- World Meteorological Organization, 2008. Guide to Meteorological Instruments and Methods of Observation: Part I.7. Measurement of Radiation. WMO. WMO-No. 8.