4. konferenca z mednarodno udeležbo
Konferenca VIVUS – s področja kmetijstva, naravovarstva, hortikulture in floristike ter živilstva in prehrane
»Z znanjem in izkušnjami v nove podjetniške priložnosti«
20. in 21. april 2016, Biotehniški center Naklo, Strahinj 99, Naklo, Slovenija

4th Conference with International Participation
Conference VIVUS – on ***Agriculture, Environmentalism, Horticulture and Floristics, Food Production and Processing and Nutrition***
»With Knowledge and Experience to New Entrepreneurial Opportunities«
20th and 21st April 2016, Biotechnical Centre Naklo, Strahinj 99, Naklo, Slovenia

Dušikovi oksidi in njihova okoljska funkcija

Marjan Senegačnik
University of Maribor, Faculty of Organizational Sciences, Slovenia, marjan.senegacnik@fov.uni-mb.si
Drago Vuk
University of Maribor, Faculty of Organizational Sciences, Slovenia, drago.vuk@fov.uni-mb.si

Nataša Petrović
University of Belgrade, Faculty of Organizational Sciences, Serbia, petrovicn@fon.rs

Izvleček
Prispevek obravnava vlogo dušikovih oksidov pri obremenjevanju okolja. Dušik in kisik sestavljata sedem različnih spojin, izmed katerih so tri spojine pomembne glede njihovih vplivov na okolje. Vendar so večkrat pri obravnavi okoljskih vplivov dušikovih oksidov prisotne nejasnosti. Namen prispevka je pojasniti različno vlogo posameznih spojin na obremenjevanje okolja. V prispevku je podan kratek pregled vseh dušikovih oksidov. Pojasnjena je razlika med onesnažili (polutanti) ter toplogrednimi plini. Nato so prikazani vplivi in značilnosti didušikovega oksida, ki je toplogredni plin, ter dušikovega oksida in dušikovega dioksida, ki sodita med najpomembnejša onesnažila (polutante). Med najbolj problematične vire emisij dušikovih oksidov sodijo dizelski motorji cestnih vozil. V prispevku so na kratko predstavljene rešitve, ki omogočajo znižanje emisij dušikovih oksidov iz avtomobilskih motorjev ter nekateri zapleti na tem področju, ki so v letu 2015 vzbudili precej pozornosti svetovne javnosti. V zaključku je na kratko omenjena tudi problematika dušikovih oksidov v Sloveniji, kjer so predvsem problematični kot prekurzorji troposferskega ozona.

Ključne besede: didušikov oksid, dušikov oksid, dušikov dioksid, pojav tople grede, obremenjevanje ozračja, avtomobilski izpušni plini

Nitrogen oxides and their environmental function

Abstract
The paper is concerned with nitrogen oxides and their role in pollution. Nitrogen and oxygen form seven different compounds, three of them are of environmental importance. It seems that often certain degree of ambiguity is present in public discussions of environmental role of nitrogen oxides. The purpose of the present paper is to explain different impact of certain nitrogen oxide compound on the environment. The paper contains brief review of nitrogen oxides. The difference between pollutants and greenhouse gases is also explained. Then are described properties and environmental impact of nitrous oxide which is greenhouse gas as well as properties and environmental role of nitric oxide and nitrogen dioxide which are among the most problematic air pollutants. Compression ignition (diesel) engines of vehicles are one of the most important sources of nitrogen oxides emissions. Therefore some technical solutions which enable lowering of nitrogen oxides emissions from automotive exhaust are briefly described as well as some incidents in this field which attracted a lot of public attention in

2015. In the conclusion also the problem of nitrogen oxides in Slovenia is briefly discussed where thse compounds seem particularly problematic as tropospheric ozone precursors.

Key words: Nitrous oxide, nitric oxide, nitrogen dioxide, greenhouse effect, air pollution, automotive exhaust.

1 Introduction

Nitrogen oxides present a group of six different compounds (or seven compounds when considering also unstable nitrogen peroxide, chemical formula NO_3). All nitrogen oxides except nitrous oxide (or dinitrogen oxide, N_2O) are highly toxic compounds. Other members of this group are nitrogen oxide (NO), dinitrogen trioxide (N_2O_3), nitrogen dioxide (NO_2), dinitrogen tetroxide (N_2O_4) and dinitrogen pentoxide (N_2O_5). Certain nitrogen oxides are stable in limited temperature range (Lazarini and Brenčič, 1984, 352). Nitrogen oxides are often considered in connection with environmental problems. However, when discussing their environmental impacts there in publicity some ambiguity can be observed. The purpose of this paper is to describe the environmental impact of nitrogen oxides.

Some properties of nitrogen oxides are shown in Table 1.

Table 1: Properties of nitrogen oxides

Formula	Name	Colour	Remarks
N_2O	Nitrous oxide/ dinitrogen oxide	Colourless	Rather unreactive
NO	Nitric oxide	Gas- colourless, Liquid and solid blue	Moderately reactive
N_2O_3	Dinitrogen trioxide	Blue solid	Extensively dissociated as gas
NO_2	Nitrogen dioxide	Brown	Rather reactive
N_2O_4	Dinitrogen tetroxide	Colourless	Extensively dissociated to NO_2, partly as liquid
N_2O_5	Dinitrogen pentoxide	Colourless gas, white solid	Unstable as gas, ionic solid
NO_3	Nitrogen peroxide	White solid	Unstable

Sources: Cotton and Wilkinson, 1972, 354; Lazarini and Brenčič, 1984, 351-355; Sharp, 277-278

2 Pollutants and greenhouse gases

Both aggravated air quality due to emissions of pollutants as well as greenhouse effect attract a lot of public attention. However, as has been mentioned above, it seems that when considering these two environmental problems in publicity is necessary to distinguish air pollution problems from greenhouse effect. It seems that these two environmental problems are sometimes confused and certain level of ambiguity can be observed in discussions.

2.1 Air pollutants

Air pollutants are substances present in the air which are noxious to humans and/or also to other living organisms. Exposure to elevated level of pollutants presents considerable health risk. These substances might be present in the air occasionally due to certain natural phenomena as are forest fires or volcanic eruptions but nowadays they are continuously present due to human sources. Concentration of pollutants in the air is subject of systematic survey for decades. The most important air pollutants are sulphur dioxide (chemical formula SO_2), carbon monoxide (chemical formula CO), hydrocarbons (abbreviation HC), particulate matter (abbreviation PM), tropospheric ozone (chemical formula O_3) and, however, nitrogen oxides (abbreviation NO_x) – which are the subject of this paper.

2.2 Greenhouse gases

The greenhouse effect is called the ability of atmosphere to absorb heath. The earth surface receives energy from the sun in the form of ultraviolet and visible light. Earth´s surface emits this radiation back. However, due to its lower temperature earth`s surface emits infrared radiation. In the atmosphere are present certain substances which can absorb infrared radiation and in this way contribute to the retention of heath in the atmosphere. This process is to certain extent natural and is necessary for the existence of the life on the earth. However, because of various human activities the quantity of infrared light absorbing substances in the atmosphere is increasing. This means that also the ability of atmosphere to absorb heath is increasing and this presents the reason for global warming. The greenhouse effect itself does not present a problem – the problem is additional greenhouse effect caused by human activities - so called anthropogenic greenhouse effect. Substances which contribute to the greenhouse effect are called greenhouse gases. Nevertheless some greenhouse gases due to their direct adverse effect on living organisms are treated also as pollutants (by example tropospheric ozone) this two effects must not be confused. Therefore, carbon dioxide, the main contributor to the anthropogenic greenhouse effect is by no means treated as pollutant.

From the environmental point of view three of nitrogen oxides are important: nitrous oxide (N_2O) which is connected with greenhouse effect and nitrogen oxide (NO) and nitrogen dioxide (NO_2) which are both important air pollutants.

3. Nitrous oxide (N_2O)

Nitrous oxide or dinitrogen oxide (N_2O) is – as it has been mentioned above – the only of nitrogen oxides that is not poisonous. Nitrous oxide is at room condition colourless gas.

This compound has been discovered by Joseph Priestly in 1772. In 1798 the analgesic effect of nitrous oxide has been observed by Sir Humphry Davy as well as the fact that inhalation of this gas causes relaxation and euphoric feeling, sometimes even eruptions of laugh. Therefore nitrous oxide is known also as laughing gas. In the first half of 19^{th} century it was pretty popular by people in Great Britain United States and Canada breathing nitrous oxide for amusement. In 1845 American dentist Horace Wells for the first time used nitrous oxide as anaesthetic. After several successful attempts his demonstration of nitrous oxide as anaesthetic at Harvard Medical School failed due to certain unfortunate circumstances. This has to certain extent slowed the use of nitrous oxide as anaesthetic. Nevertheless, it was later successfully used by other dentists. In 1864 Wells was recognized as the inventor of anaesthesia by American Dental Association and 1870 also by American Medical Association. In the meantime also other, stronger anaesthetic agents as are ether and chloroform were introduced. However, nitrous oxide is nowadays still widely used as sedative and mild but very save anaesthetic agent in both dentistry and medicine (http://www.sedationdentistry4u.com/nitrous-oxide-sedation-history.htm, 20.02.2016)

As nitrous oxide is not poisonous it is, of course, not treated as pollutant. Nevertheless, due to its capability of absorbing infrared radiation it is acting as greenhouse gas and therefore their emissions are not completely unproblematic from the environmental point of view. Nitrous oxide emissions contribute about 5 per cent to the entire anthropogenic greenhouse effect (Botkin and Keller, 2003). Nitrous oxide is present in atmosphere from natural sources due to nitrogen cycle. However, problematic are additional emissions into the atmosphere caused by human activities and this derive mainly from the use of fertilizers in agriculture (75 per cent of emissions), other important sources are industry (production of nylon fibres and nitric acid, the latter is also to a significant extent connected with production of synthetic fertilizers) and automotive emissions. The contribution of various sources to nitrous oxide emissions is shown in Figure 1
(http://www3.epa.gov/climatechange/ghgemissions/gases/n2o.html, 20.2.2016).

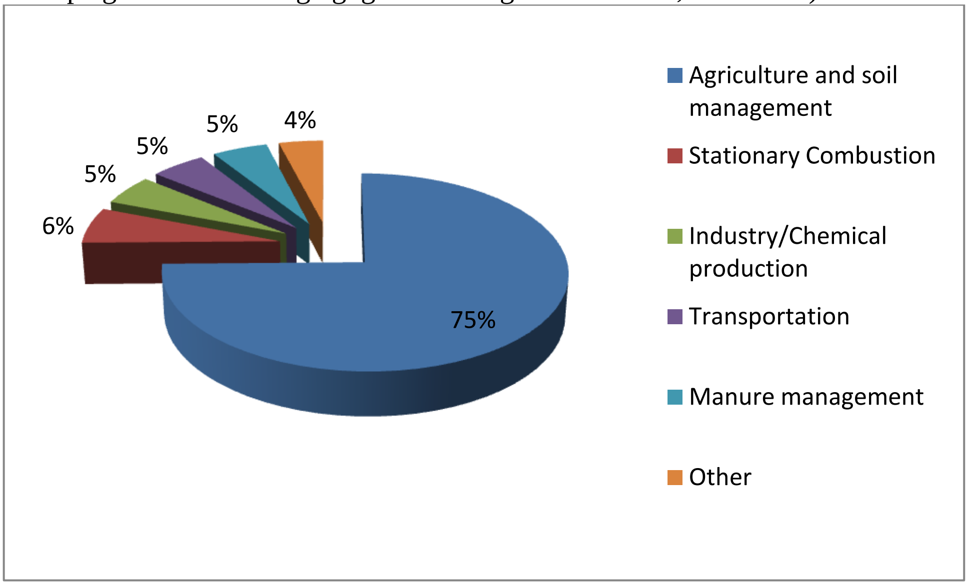

Figure 1: Sources of nitrous oxide emissions into atmosphere.

Source: http://www3.epa.gov/climatechange/ghgemissions/gases/n2o.html, 20.2.2016

4. Nitric oxide (NO) and nitrogen dioxide (NO_2)

Contrary to the non-toxic nitrous oxide both nitric oxide (NO) and nitrogen dioxide (NO_2) are poisonous compounds and are among the most important air pollutants. Their presence in the air can derive from various origins, however, thermal power plants and traffic (automotive exhaust) presents the most important source of these two nitrogen oxides. They are often considered together and are designated abbreviated as NO_x.

Nitric oxide (NO) is at normal conditions colourless gas. Nitric oxide is synthesised by high temperatures (by example during combustion in the engine) from nitrogen and oxygen which are constituents of air. Nitric oxide plays certain role in human metabolism where it shows vasodilationing effect (Abrams, 1996). However, its concentrations are recommended to be kept bellow 25 ppm (30 mg per m^3). At higher concentrations irritating effects on eyes, skin and respiratory system can be observed. Concentrations of NO above 100 ppm are immediately dangerous for life (http://www.cdc.gov/niosh/npg/npgd0448.html , 27.2.2016).

In air nitric oxide is oxidized to nitrogen dioxide. Nitrogen dioxide is at normal conditions brown gas. Nitrogen dioxide is poisonous gas which affects particularly respiratory tract. Exposure to nitrogen dioxide can lead to respiratory problems and lungs function decrease (http://www.euro.who.int/__data/assets/pdf_file/0005/112199/E79097.pdf, 28.2. 2016). Besides direct adverse effects nitrogen dioxide is problematic also as precursor of tropospheric ozone and acid rain.

Contrary to nitrous oxide nitrogen dioxide does not have an important direct greenhouse effect. However, as precursor of tropospheric ozone it contributes indirectly to global warming.

5. NO_x emissions from automotive exhaust and their lowering

As has been mentioned above the most important source of nitric oxide and nitrogen dioxide in the air are automotive emissions. The NO_x emission control (like other pollutants from automotive sources: hydrocarbons, carbon monoxide and particulates) has attracted a lot of attention in previous decades. However, it should be emphasized that nitrogen oxides emission control is much easily performed in the case of spark ignition (Otto) engines than in the case of compression ignition (Diesel) engines.

Spark ignition engines operate at almost stoichiometrical (theoretical) air-fuel mixture. At such conditions reduction of nitrogen oxides to nitrogen can be achieved simultaneously with oxidation of carbon monoxide and hydrocarbons to carbon dioxide. This is the concept of operation of three-way catalytic converters which have been introduced in United States in 1981 and in the Europe in the beginning of 1990s. Three-way catalytic converter enables relative efficient control of nitrogen oxides emissions.
5.2 Selective catalytic reduction
Much different is situation in the case of compression ignition (Diesel) engines. Diesel engines operate at considerable excess of air in the mixture. Three-way catalytic converters are not efficient in such conditions. Therefore, NO_x emission control is much more complicated task in the case of compression ignition engines. Oxidizing catalytic converters have been used exclusively by Diesel engines for certain number of years. However, as legislative demands are becoming increasingly more restrictive also additional reducing catalytic converters have become necessary. There exist three different principles of NO_x emissions lowering (Yang et al., 2015):

- Lean NO_x trap (LNT)
- Selective catalytic reduction (SCR) and
- Exhaust gas recirculation (EGR).

5.1 Lean NO_x trap (LNT)

Lean NO_x trap (lean nitrogen oxides trap, abbreviated LNT) operates as some kind of filter as nitrogen oxides under normal diesel engine operation (lean conditions) are adsorbed on a catalyst like in a trap. However, the catalyst becomes rapidly saturated and needs regeneration. Regeneration is achieved with periodical injections of rich fuel mixture where catalytic reduction of nitrogen oxides is performed. This contributes to the increased fuel consumption. In the case of high engine loading LNT capacity is often insufficient which is leading to increased NO_x emissions (Yang et al., 2015). The LNT system consists of oxidizing catalyst (usually platinum), adsorbent (barium oxide or some other metal oxide) and reducing catalyst (rhodium) (http://product-finder.basf.com/group/corporate/product-finder/en/brand/BASF_LNT, 28.2.2016). The position of LNT trap in the vehicle exhaust system and its operation principle are shown in Figure 2.

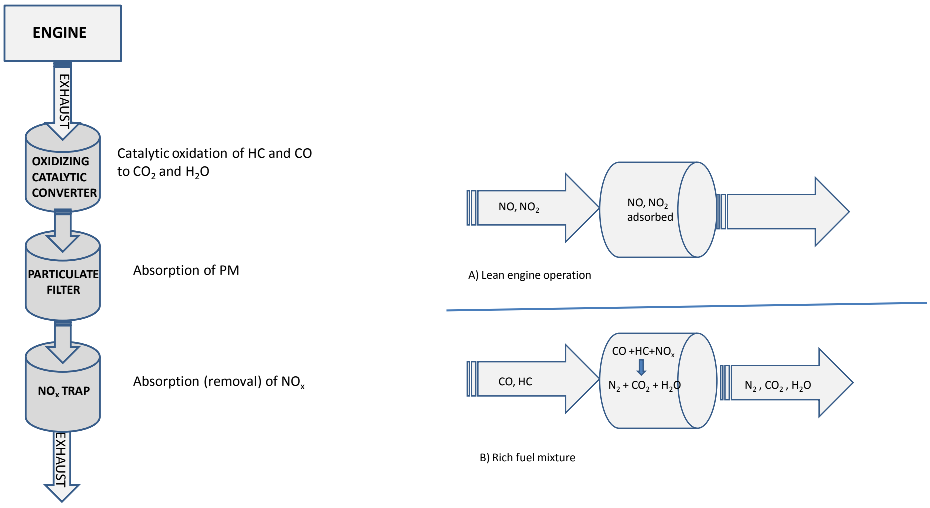

Figure 2: Lean NO_x trap position in automotive exhaust system and its operation principle
Source: Russel et al., 2015, http://product-finder.basf.com/group/corporate/product-finder/en/brand/BASF_LNT)

5.2 Selective catalytic reduction (SCR)

Alternative mode of NO_x emissions lowering presents selective catalytic reduction (abbreviated SCR). The basic principle of this method is that nitrogen oxides are catalytically reduced with ammonia to nitrogen and water vapour is formed as by product. This method has been used in non-mobile devices originally (Yang et al, 2015; Sinzenich et al., 2014).

$$4\,NO + O_2 + 4\,NH_3 \rightarrow 4\,N_2 + 6\,H_2O$$

$$NO + NO_2 + 2\,NH_3 \rightarrow 2\,N_2 + 3\,H_2O$$

However, ammonia (in gaseous form or as aqueous solution) has been due to safety reasons substituted with aqeous solution of urea. Urea acts as precursor of ammonia but also as reducing agent itself (Ghosh et al, 2013). This method demands equipping of vehicle with an additional tank for urea solution.

$$2\,CO(NH_2)_2 + 6\,NO \rightarrow 5\,N_2 + 2\,CO_2 + 4\,H_2O$$

$$4\,HNCO + 6\,NO \rightarrow 5\,N_2 + 4\,CO_2 + 2\,H_2O$$

Schematic drawing of SCR system is shown in Figure 3.

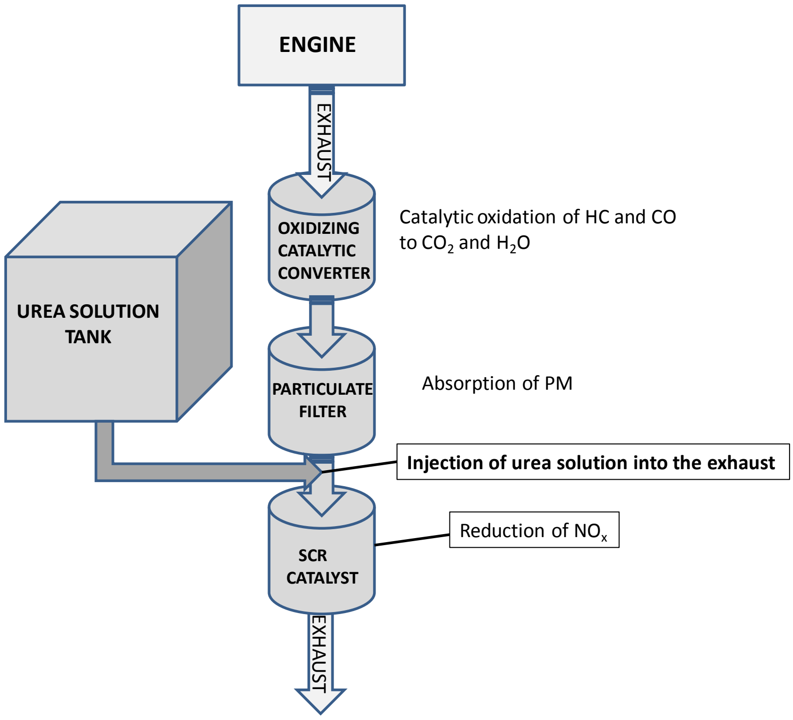

Figure 3: Schematic drawing of Selective catalytic reduction system for vehicle exhaust treatment (http://www.dieselforum.org/about-clean-diesel/what-is-scr , 16.1.2016)

5.3 Exhaust gas recirculation (EGR).

The third possibility is recirculation of exhaust gases (abbreviated EGR)– a certain part of exhaust gases is driven back into the engine. This enables lowering of combustion temperature and lowering the intensity of nitrogen oxide synthesis. However, EGR method establishes certain weaknesses as are low efficiency at high engine loading, increased fuel consumption and more intense soot particles formation (Yang et al., 2015; Zheng et al., 2004). The principle of EGR system is shown in Figure 4.

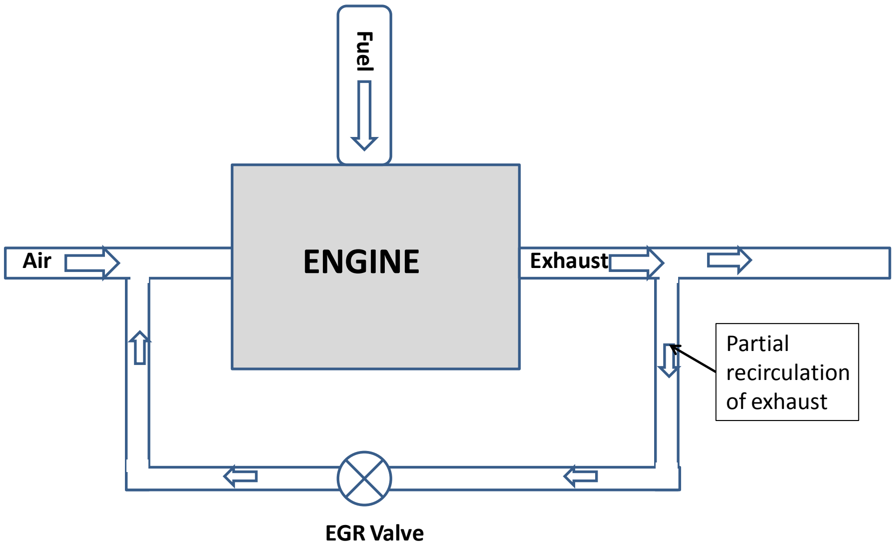

Figure4: Exhaust gas recirculation system (Zheng et al., 2004).

When considering cars with diesel engine on the European market it can be observed that EGR is seldom used. Some manufacturers prefer LNT meanwhile others SCR technology. LNT is more convenient for smaller engines (< 2,0 litres) and SCR for larger (> 2,0 litres) engines (Yang et al., 2015).

6. Emissions standards and related problems

As control of nitrogen oxides by compression ignition engines is more complicated than in the case of spark ignition engines therefore also somewhat higher emissions are allowed for diesel engines. Nevertheless, the legislative demands become increasingly more restrictive. Euro 3 standard in 2000 permits for personal cars 0,50 g of NO_x per kilometre meanwhile Euro 6 from 2014 has lowered the limit on 0,080 g/km (https://www.dieselnet.com/standards/eu/ld.php, 17.1.2016). American standard (US EPA Tier 2/Bin 5 or California LEV –II ULEV) is still more restrictive (0,043 g/km) (http://transportpolicy.net/index.php?title=US:_Light-duty:_Emissions#Tier_2 , 17.1.2016). The trends of gradually lowering emissions limits can be seen from Figure 5.

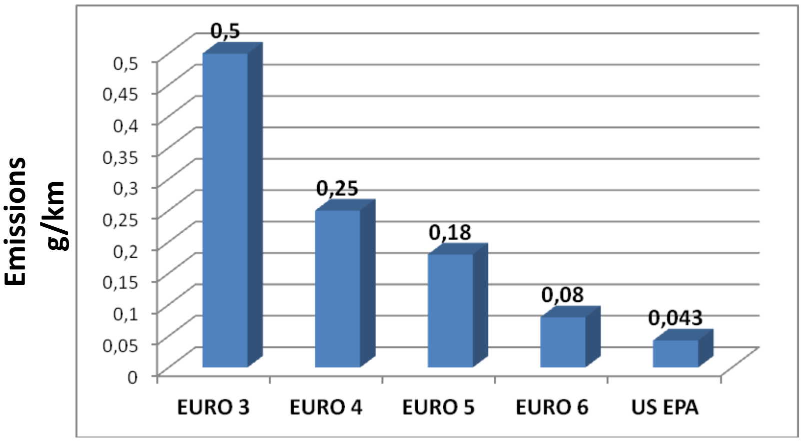

Figure 5: Nitrogen oxides emissions limits for EURO standard series and EPA Tier 2/Bin 5 standard
Sources: https://www.dieselnet.com/standards/eu/ld.php,
http://transportpolicy.net/index.php?title=US:_Light-duty:_Emissions#Tier_2

Lowering of emissions is possible due to technological development. However, low levels of nitrogen oxides in the exhaust are achieved on the expense of poorer vehicle performance capacity and higher fuel consumption. Higher fuel consumption is, naturally, undesired from the economic but also from the environmental (greenhouse gases emissions) point of view. This was probably the reason for the Volkswagen scandal which erupted in United States in 2015. Vehicles which have successfully passed highly demanding official tests showed during on road measurements much higher NO_x emissions as should happen according to testing results. Later it has been found that vehicles were equipped with special software. This software can recognize when vehicle is on emission testing and lower emission mode is switched on. During normal road driving low emission mode is switched off allowing better vehicle performances and lower fuel consumption (Russell, 2015). There have been observed some problems of on road emissions also by diesel cars of some other manufacturers.

7. Conclusion

Nitrogen oxides are substances of considerable environmental impact. Nitrous oxide has no polluting effect however its contribution to the entire anthropogenic greenhouse effect should be not neglected. Nitric oxide and nitrogen dioxide are considered among the most important air pollutants. Their emissions are connected mainly with the automotive exhaust. When regarding reports for the air quality in Slovenia in 2015 it can be considered (ARSO, 2015) that still more than nitric oxide and nitrogen dioxide themselves they are problematic as precursors of tropospheric ozone. Ozone presents besides particulates the most problematic air pollutant in Slovenia. Therefore it is important to take care of efficient nitrogen oxides emission control particularly as a way of tropospheric ozone levels control.

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