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# Editorial

As we are in the world economical crisis it seems that the similar situation is also at our journal. Last year less than 10 manuscripts received to be published in the *International Journal of Sanitary Engineering Research*. Some of them have been not accepted, and a few of them are still in the review process.

This issue deals with the professional papers only. Our readers may find practical experiences and know-how in sanitary and environmental engineering. First article is dealing with the PVC in built environment. PVC material of the frames in the windows and doors contain phthalates which is releasing into the environment. A number of studies show association between phthalates and asthma, allergies and respiratory effects. The connection between phthalates and cancer is also presented in this paper. In the case of fire the PVC releases hydrogen chloride gas and other harmful combustion products including well known deadly poison dioxin. Therefore the Slovenian government does not support the installation of PVC windows and doors in our homes and in the public buildings. We are also obliged to preserve our health and health of our children. This is particularly important at the drinking water. Slovenia is one of the rare countries where the drinking water from the water supply systems is still safe. But in many cases the drinking water is treated before use. Dangerous microorganisms in drinking water must be destroyed before this water enters the water supply system. As it is described in the paper titled '*The Generation of Chlorine Dioxide for drinking water treatment*' several methods exist for the drinking water treatment. There are described three processes for generating the pure chlorine dioxide in the drinking water. The most important step is generating high concentration of the  $Cl_2O_2$  which accelerated the final reaction to  $Cl_2$  and  $Cl^-$  which oxidize the microorganisms in the water. Another well known method is generation of the chlorine dioxide by the chemical reaction of sodium peroxodysulphate with the sodium chlorite, which creates more stable chloride solutions in a pH neutral milieu. Readers may study the chemical reactions and learn the procedures in order to choose the right drinking water treatment process in order to minimize negative impact to the human health.

The last paper describes the negative impact on the environment during transporting vehicles in automobile terminal in the Koper port. In this case authors made the appropriate tests and measurements in site. The real carbon footprint of Koper port is therefore several times higher of the theoretically calculated. To decrease the emissions produced at the vehicles transportation the additional research are necessary, but there is a very low possibility to improve the situation. We can only wait to the electrical cars or cars powered by the hydrogen or any other environment sound fuel. But this is already another story.

Sincerely,

Janez Petek  
Editor-in-Chief

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# Health concerns of PVC materials in the built environment

M. DOVJAK<sup>1\*</sup>, Ž. KRISTL<sup>1</sup>

## ABSTRACT

The objective of the paper is to investigate the influence of PVC use in the form of building materials and to draw attention to the problems connected with the exposure of people to PVC emitted phthalates in indoor environment. A systematic literature review is focused on health concerns associated with use of PVC building materials in everyday life and in extraordinary circumstances. The overview of studies indicates that the use of PVC in indoor environment has adverse health effects. A number of studies show association between phthalates and asthma, allergies and respiratory effects. A number of studies also focused on carcinogenic effect and impact of PVC on reproductive system. The most exposed population is young children and certain groups of adults during occupational exposure. The overview of studies on the influence of PVC materials in case of fire shows that when burning, PVC releases hydrogen chloride gas and other harmful combustion products. As a result, a list of recommendations for healthier built environment is systematically unfolded. Recommendations include actions during the whole life cycle of PVC material. Among them the most important are: adoption and implementation of regulations and standards on the marketing and use of phthalates in building materials; production and use of safer alternatives; fire safety and implementation of waste management. Further measurements of phthalate release from PVC building materials and additional research of health impacts are needed to achieve a uniform opinion about health risks associated with phthalates.

## KEY WORDS:

PVC materials, phthalates, health concerns, fire, combustion products.

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## 1. INTRODUCTION

Polyvinyl chloride (IUPAC name: polychloroethanediyl, hereinafter PVC) is a thermoplastic polymer and one of the most widely used materials in our everyday life. PVC is present in a large variety of products, due to simple moulding, firmness and inexpensiveness [1]. For example floor furnishing, window frames, food wraps, hair gel, shampoo, paper clips, credit cards, automobile seats and toys are just some of the items that contain PVC. European PVC organisation [1] states that on the global level, demand for PVC exceeds 35 million tonnes per year and it is in constant growth (+5 % on global, average), with higher growth rates in the developing countries. In Europe (EU-27), the production of PVC products – including exports – totals about 8 million tons per year. European PVC resin consumption totals some 6.5 million tons per year, or 15 % of all plastics use in Europe, with an average growth of 2 %-3 % per year [1]. PVC is widely used in various industries, such as food, agricultural, pharmaceutical, cosmetic, automotive, toy, and construction industry which consume the largest amount of PVC. As building material it is mainly used for final furnishing or coating of ceilings, walls and floors, carpentry products (i.e. windows and doors), facade elements, roofing materials and installations (i.e. piping and cabling). Plastic pipes and construction uses account for 75 % of all PVC consumption in North America and 50 % in Western Europe. Construction is also the fastest growing PVC sector, with a projected annual average growth rate of 3.5 % between 2002 and 2007 [2].

Widespread production and use of PVC materials results in problems related to wastes. The amount of waste plastic generated in Europe (EU-27) in 2006 was 14,647,803 tones; in Slovenia this amount reached 43,486 tones. According to Eurostat [3] the amount of waste plastic generated in EU-27 in 2006 increased by 22 % compared to 2004. In Slovenia the increase rate was 12 %. The majority of waste plastic in EU as well as in Slovenia was generated by industry. Households, however, are responsible for approximately 15 % of the overall generated waste plastic in EU-27; the percent strongly varies depending on the country. Concerning is the information that the amount of waste packaging in 2006 in Slovenia had an increasing rate (by 14 % for industry; 6 % for households) compared to 2004. The amount of waste plastic in construction and demolition in EU-27 in 2006 had increasing rate, i.e. from 3 % (Denmark from 1,513 tones to 1,556 tones) to 98 % (from 2 tones to 82 tones in Bulgaria) compared to year 2004. We have to point out that uncontrolled stages of waste management may result in potential health concerns as well as environmental problems. In Slovenia the rate of waste plastic generated in construction and demolition had a decreasing rate; in 2004, 592 tones were generated, in 2006 this amount fell to 365 tones. The waste material has to be managed - reused, recycled, incinerated or disposed. The amount of recycled plastic in EU-27 in 2006 was 6,428,648 tones; in Slovenia this amount was 22,274 tones (12,193 tones in 2004).

European PVC resin consumption totals some 6.5 million tons per year, or 15 % of all plastics use in Europe, with an average growth of 2 %-3 % per year.

Because there is no covalent bond between phthalates and the PVC, the phthalates are easily released from PVC materials into the environment. Phthalates migrate during the whole life cycle of the product (from production to final disposal).

At the first stage in the PVC production process ethylene and chlorine are combined to produce an intermediate product called ethylene dichloride; this is then transformed into vinyl chloride, the basic building block of polyvinyl chloride or PVC. The process of polymerisation links together the vinyl chloride molecules to form chains of PVC. The PVC produced in this way is in the form of white powder. It is not used alone, but blended with other ingredients. To increase the flexibility, transparency, durability and longevity of PVC softeners and plasticizers are added during the production. Phthalates (or phthalate esters) are esters of phthalic acid and are the most common type of general plasticisers. The most widely used phthalates are di-2-ethyl hexyl phthalate (DEHP), diisodecyl phthalate (DIDP), diisononyl phthalate (DINP), and benzylbutylphthalate (BBP). PVC formulations can be shaped by a variety of techniques and, using very little energy, are made into the final product form [1].

In the developed countries people spend 90 % of time indoors [4]; therefore the quality of indoor environment is extremely important. PVC building materials and everyday products often deteriorate indoor air quality. Because there is no covalent bond between phthalates and the PVC, the phthalates are easily released from PVC materials into the environment [5]. Phthalates migrate during the whole life cycle of the product (from production to final disposal). They are subject to photo-degradation, biodegradation, and anaerobic degradation and thus generally do not persist in the outdoor environment [6]. However, their lifespan in indoor environment is relatively long. Exposure to emitted phthalates may cause the adverse effects on human health [7]. The earliest research about their adverse effects on human health goes back to 1976, when Šarič et al. [8] published the article about malignant tumours of the liver and lungs in an area with the PVC industry. Public health concerns about phthalate plasticizers have been growing over the last few years.

Worldwide and as well as in Slovenia public awareness on the use of PVC materials and phthalates for toys, childcare articles and also cosmetic products is quite high. Proven human toxicity with animal and human studies results in restriction of selected phthalate esters in toys and childcare products. Although the same phthalates are used in PVC building materials, there is no restriction for these products. Furthermore there is no general consensus what kind of PVC products and what type of phthalates should be prohibited in buildings. Additionally, health impacts of PVC building materials are still widely unknown. The objective of the paper is to investigate the influence of PVC building materials on human health and to draw attention to the problems connected with the use of PVC and phthalates in indoor environment. A systematic literature review focuses on health concerns associated with PVC building materials in everyday life and in extraordinary circumstances, i.e. in case of fire. Main concerns are defined and recommendations for the prevention of negative health effects of PVC building materials are systematically unfolded.



## 2. METHODS

For literature review and selection criteria there were searched Pub Med and Science Direct for peer-reviewed publications from 1976 to 2011 written in English, with the keywords “PVC”, “plasticizers”, “phthalate esters”, “endocrine disruptors”, “DINP”, “DEHP”, “DIDP”, “DBP”, “BBP”, together with “health”, “adverse health effects”, “health hazard”, “toxicology”, “phthalate metabolites”, “occupational exposure”, “environmental impact”, “indoor dust”, “asthma”, “allergies”, “fire”, “combustion products”, “dioxins”, “carbon monoxide”, “carbon dioxide”, “soot”, “hydrogen chloride”, “threshold limit values”. There were reviewed reports of European PVC organization; European Council for Plasticisers and Intermediates; European Food Safety Authority; International Labour Organization; International Occupational Safety and Health Information Centre; Centres for Disease Control and Prevention; World Health Organization; Institute of Public Health of the Republic of Slovenia; U.S. Green Building Council; Environmental Protection Agency United States. There were also reviewed regulations of the European Parliament; and chemical data of Occupational Safety and Health Administration; National Institute for Occupational Safety and Health; American Conference of Governmental Industrial Hygienists; UK Health Protection Agency; and articles of U.S. Centre for the Evaluation of Risks to Human Reproduction; U.S. Centre for Health, Environment and Justice. We also searched the above keywords with the Google search engine and publications of University of Ljubljana with the Cobiss online bibliographic system.

Legal aspects on the use of PVC were searched and analysed. Findings of studies were compared to regulations and guidelines. The findings of the comparative study enabled us to define the main problems associated with the use of PVC building materials and were the basis for the development of recommendations for prevention of negative health effects of PVC building materials. They include the actions regarding the whole life cycle of PVC material with the emphasis on the use of PVC materials in buildings during their product use phase.

The findings of the comparative study enabled us to define the main problems associated with the use of PVC building materials.

## 3. RESULTS

### 3.1 Results of the state-of-art analysis

Results of the state-of art analysis include the main findings in literature review. The results are presented regarding the field of influence: health concerns associated with phthalate exposure in everyday life; phthalate exposure and risk of asthma and allergies in adults and children; health concerns associated with building materials; health concerns of PVC building materials in case of fire.

#### 3.1.1 Health concerns associated with phthalate exposure in everyday life

Various studies have concluded that phthalates may be endocrine disruptors [5,9,10]. Council of European Union [11] defined endocrine dis-

A number of studies showed the association between phthalates and asthma, allergies, or related respiratory effects.

rupters as substances that act like hormones and disturb the normal functioning of the endocrine system. The endocrine system is a network of glands and hormones that regulate many of the body's functions, including growth, development and maturation. Endocrine disrupters are suspected of interfering with the production and performance of hormones. Such effects have already been seen at animals, like impairing reproduction, development or immunity. People may be exposed to phthalates among others through food, plastic products, paints and cosmetics. These chemicals are thought to be responsible for low testosterone level, declining sperm counts and quality, genital malformations, retarded sexual development or even reproductive abnormalities and increased incidences of certain types of cancer [5,9-11].

Health concerns related to phthalates exposure have focused primarily on cancer and reproductive effects [5,7,9,10]. However, plastic building materials present a potential chemical emission source in indoor air [12]. A number of studies [7,13-19] showed the association between phthalates and asthma, allergies, or related respiratory effects. Their health impact depends on the type of phthalate ester, dose, exposure time (i.e. short-term or acute exposure, long-term, repeated exposure or chronic exposure) and individual characteristics (gender differences and anthropometric characteristics, age, cultural differences, and health status) [20]. European Council for Plasticizers and Intermediates [21] classify the phthalate plasticizers according to their health impact (i.e. cancer, fertility and developmental effects). **Table 1** summarizes the current classification and labelling of phthalates adopted in March 2001 [21,22].

According to the type of phthalate ester there are several routes of exposure. For example di(2-ethylhexyl) phthalate (DEHP), diethyl phthalate (DEP), diisononyl phthalate (DINP), dibutyl phthalate (DBP) can be absorbed into the body by inhalation, by ingestion, and through the

**Table 1:**  
Classification and labelling of phthalate plasticizers [21,22].

Phthalate ester	Cancer	Fertility	Developmental
DBP <sup>1</sup>	None	Category 3	Category 2
DEHP <sup>2</sup>	None	Category 2	Category 2
DINP <sup>3</sup>	None	None	None
DIDP <sup>4</sup>	None	None	None
BBP <sup>5</sup>	None	Category 3	Category 2 proposed

<sup>1</sup>dibutyl phthalate

<sup>2</sup>di(2-ethylhexyl) phthalate

<sup>3</sup>diisononyl phthalate

<sup>4</sup>diisodecyl phthalate

<sup>5</sup>benzylbutyl phthalate

Category 1 – Substances known to cause effects in humans. Based on epidemiological data. Skull and crossbones. Category 2 – Substances to be regarded as if they cause effects in humans. Based on clear evidence in animal studies. Skull and crossbones. Category 3 – Substances causing concern for humans. Based on sufficient evidence in animal studies to cause suspicion. St. Andrews Cross.

skin. The routes of exposure for diallyl phthalate (DAP) are by inhalation of its aerosol and by ingestion, and for diisobutyl phthalate (DIBP) through skin and by ingestion. Diisodecyl phthalate (DIDP) can be absorbed into the body only by inhalation of its vapour [23-28]. Harmful effects depend on the type of phthalate ester as well as exposure time and dosage. Effects of short-term exposure of phthalate esters may include eye irritation (i.e. DIDP, DEHP), skin irritation (i.e. DIDP), irritation of respiratory tract (i.e. DEHP), or even chemical pneumonitis (i.e. DAP). Long-term or repeated exposure may have effects on the liver (i.e. DIDP) [25], on the testicles (i.e. DEHP) [24], or may even cause skin sensitization (i.e. DAP) [23].

Animal tests show that DEHP and DIBP possibly cause toxicity to human reproduction or development [23,24]. DEP may be hazardous to the environment with a moderate acute toxicity to aquatic life [23]. According to European Union Risk Assessment Report [28] and International Labour Organization [26] DBP is probably carcinogenic to humans. Even though no adequate long-term toxicity and/or carcinogenicity studies in animals as well as humans are available, DBP is classified and labelled according to the 28<sup>th</sup> ATP of Directive 67/548/EEC4 [29]: DBP is a substance that is classified as health hazard with Repr. Cat. 3 (Category 3, Reproductive toxins)<sup>1</sup>, and labelled with risk phrases R63 (may cause harm to the unborn child), R62 (possible risk of impaired fertility), and R50 (dangerous for the environment, very toxic to aquatic organisms) [26,28].

Once phthalates enter a person's body, they are converted into breakdown products (metabolites) that pass out quickly with urine and may cause an adverse health effect [30]. Romero-Franco et al. [31] investigated personal care product use and urinary levels of phthalate metabolites in Mexican women. The study concluded that certain personal care products such as body lotion and deodorant showed higher urinary concentrations of some DEHP metabolites. Urinary concentrations of phthalate metabolites showed a positive relationship with the number of products used. Guo et al. [32] found out that Chinese population is widely exposed to phthalates. Children are exposed to higher levels of DEHP and lower levels of DEP and DEP than the adults. Additionally, study on Danish children [33] concluded that the youngest children, especially boys were the most exposed. The highest exposure levels were found for DEHP and DBP. However, biomonitoring studies on levels of phthalate metabolites enable us to estimate the daily intake of phthalates and can determine whether people have been exposed to higher levels. A tolerable daily intake (TDI) is an estimate of the amount of substances in air, food or drinking water that can be taken in daily over a lifetime without appreciable health risk. TDI values for phthalates are presented in the **Table 2** [34-36].

Once phthalates enter a person's body, they are converted into breakdown products (metabolites) that pass out quickly with urine and may cause an adverse health effect

<sup>1</sup> Chemicals that produce or increase the incidence of non-heritable effects in progeny and/or the impairment in reproductive functions or capacity.

Epidemiologic studies at children evidenced that the presence of PVC flooring and walls was related with asthma, rhinitis, wheeze, cough, phlegm, nasal congestion, nasal excretion and eczema.

**Table 2:**

Tolerable Daily Intake (oral) for selected phthalate esters [34-36].

Phthalate	TDI (Tolerable Daily Intake)
DEHP <sup>1</sup>	37 µg/kg body weight/day
DBP <sup>2</sup>	0.01 mg/kg body weight /day
DINP+DIDP <sup>3</sup>	0.15 mg/kg body weight /day
DEP <sup>4</sup>	5 mg/kg body weight /day

<sup>1</sup>di(2-ethylhexyl) phthalate

<sup>2</sup>dibutyl phthalate

<sup>3</sup>diisononyl phthalate+diisodecyl phthalate

<sup>4</sup>diethyl phthalate

### 3.1.2 Phthalate exposure and risk of asthma and allergies in adults and children

Jaakkola and Knight [19] reviewed the evidence for the role of exposure to phthalates from PVC products in the development of asthma and allergies. The systematic review and meta-analysis are based on 27 human and 14 laboratory toxicology studies (1950 to May 2007). The studies in adults assessed the relationship between PVC-related occupational exposure (meat wrappers, hospital and office workers, fire fighters, PVC processors) and the risk of asthma, allergies, or related respiratory effects [13-15], and one of the studies [18] also examined the role of home exposures. Exposure to phthalates (inhalation exposure to pyrolysis products of PVC, burning PVC) and PVC materials (damaged PVC floor, wall paper) caused the increased prevalence of respiratory symptoms, including shortness of breath, wheezing and chest pain, as well as increased occurrence of upper respiratory symptoms (dry or sore throat, stuffy or runny nose, coughing, chest tightness) and eye symptoms (burning, itchy, or tearing eyes) and acute respiratory tract illness (pleurisy, bronchitis, and pneumonia). However, study by Tukiainen [37] found out that PVC materials by themselves do not evoke immediate asthmatic reactions. The appearance of respiratory symptoms depends upon the health status of the exposed subject and exposure time (i.e. acute or chronic exposure). In the study 10 subjects were experimentally challenged to the degraded PVC products under controlled conditions. All the subjects had previously experienced respiratory symptoms suspected to be caused by this kind of exposure in their work place. Five subjects had doctor-diagnosed asthma. After the PVC exposure, subjects reported respiratory tract symptoms significantly more often than they did after the control test.

Epidemiologic studies at children [7,16,17] evidenced that the presence of PVC flooring and walls was related with asthma, rhinitis, wheeze, cough, phlegm, nasal congestion, nasal excretion and eczema. These findings underline the need to consider the health aspects of materials used in indoor environment. Infants are especially sensitive to the health impacts of phthalates, mainly due to their lower body weight, higher activity levels and age-related behavioural characteristics. Jaak-

kola et al. [7] assessed the role of PVC and textile materials in the home in the development of bronchial obstruction in infants in Oslo, Norway (during the first 2 years of life). The risk of bronchial obstruction was related to the presence of PVC flooring and textile wall materials. Emissions from plastic materials indoors may have adverse effects on the lower respiratory tracts of small children. Similar conclusion was also made by Jaakkola et al. [16]. Lower respiratory tract symptoms – persistent wheezing, cough, and phlegm were strongly related to the presence of plastic wall materials, whereas upper respiratory symptoms were not. The risks of asthma and pneumonia were also increased in children exposed to such materials.

### 3.1.3 Health concerns associated with building materials

Dust concentrations of different phthalate esters are related to building materials. Bornehag et al. [17] found associations between dust concentrations and the amount of polyvinyl chloride (PVC) used as flooring and wall material in homes. Furthermore, high concentrations of n-butyl benzyl phthalate (BBzP) and di(2-ethylhexyl) phthalate (DEHP) (above median) were associated with water leakage in homes (due to degradation of PVC floors caused by moisture/water and, in some cases, highly basic moist concrete surfaces), and high concentrations of DEHP were associated with buildings constructed before 1960. Both BBzP and DEHP were found in buildings without PVC flooring or wall covering, but were consistent with numerous other plasticized materials that are anticipated to be present in a typical home. Phthalates and adhesives in PVC materials may react with moisture in constructional complexes and form products that cause odours in indoor air as well as sick building syndrome. Chino et al. [38] found out that moisture with high pH in concrete slabs and self-levelling sub-flooring material reacts with di-2-ethylhexyl phthalate (DEHP) in the polyvinyl chloride (PVC) flooring and compounds containing the 2-ethyl-1-hexyl group in the adhesive. In such way 2-ethyl-1-hexanol (2E1H) is formed, which was detected in indoor air at relatively high concentrations. One of the most common problems related with constructional complexes in old buildings is mould. Jaakkola et al. [19] found out that the risk of asthma was related to the presence of plastic wall materials and wall-to-wall carpeting, the latter in particular in the presence of mould. The use of floor-leveling plaster in homes was also a determinant of onset of asthma. These findings underline the need to consider the health aspects of materials used for floor and wall coverings, and other indoor surfaces.

### 3.1.4 Health concerns of PVC building materials in case of fire

The main cause of injury and death in fires is exposure to toxic fire effluent (smoke and gases), while the next most important cause is exposure to heat. Material safety data sheet [39] characterises PVC as a combustible material, with melting point at 75 °C. During combustion it forms hazardous products such as carbon monoxide (CO), carbon dioxide (CO<sub>2</sub>), hydrogen chloride (HCl), hydrochloric acid (a solution of HCl in water), dioxins (halogenated organic compounds), smoke/soot etc.

Emissions from plastic materials indoors may have adverse effects on the lower respiratory tracts of small children.

[40]. The characteristics, exposure limits and health impacts for the most important PVC combustion products are presented below.

Carbon monoxide is a toxic gas, but, being colourless, odourless, tasteless, and initially non-irritating, it is very difficult for people to detect [41]. It is produced from the partial oxidation of carbon-containing compounds. Carbon monoxide mainly causes adverse effects in humans by combining with haemoglobin to form carboxyhaemoglobin (HbCO) in the blood. This prevents oxygen binding to haemoglobin, reducing the oxygen-carrying capacity of the blood, which leads to hypoxia. Occupational exposure limits defined by Occupational Safety and Health Administration (OSHA) [41], National Institute for Occupational Safety and Health (NIOSH) [42] and American Conference of Governmental Industrial Hygienists (ACGIH) [43] are presented in the **Table 3** [41-45]. The acute effects produced by carbon monoxide in relation to ambient concentration in parts per million and the portion in % are listed below (**Table 4**) [41].

Carbon dioxide is colourless and odourless gas. It is felt by some to have a slight, pungent odour and biting taste [46]. At standard temperature and pressure, the density of carbon dioxide is 1.98 kg/m<sup>3</sup>, which is about 1.5 times higher than air. Carbon dioxide is an asphyxiant. It initially stimulates respiration and then causes respiratory depression. High concentrations result in narcosis. Occupational exposure limits defined by U.S. Environmental protection Agency (U.S. EPA), American Society of Heating, Refrigerating and Air-Conditioning Engineers (ASHRAE), NIOSH, OSHA, ACGIH are presented in the **Table 5** [42,43,46,47]. The acute effects produced by carbon dioxide in rela-

**Table 3:**  
Occupational exposure limits for carbon monoxide [41-45].

Occupational exposure standards	Exposure limits
OSHA PEL (United States, 11/2006) <sup>1,2,3</sup>	TWA: 55 mg/m <sup>3</sup> , 8 hour(s)
OSHA PEL 1989 (United States, 3/1989) <sup>1,2,3</sup>	TWA: 43 mg/kg (50 ppm) 8 hour(s) CEIL: 229 mg/m <sup>3</sup> CEIL: 177 mg/kg (200 ppm) TWA: 40 mg/m <sup>3</sup> , 8 hour(s) TWA: 31 mg/kg (35 ppm) 8 hour(s)
NIOSH REL (United States, 6/2009) <sup>4,5</sup>	CEIL: 229 mg/m <sup>3</sup> CEIL: 177 mg/kg (200 ppm) TWA: 40 mg/m <sup>3</sup> , 10 hour(s). TWA: 31 mg/kg (35 ppm) 10 hour(s)
ACGIH TLV (United States, 2/2010) <sup>6,7</sup>	TWA: 29 mg/m <sup>3</sup> , 8 hour(s) TWA: 22 mg/kg (25 ppm) 8 hour(s)

<sup>1</sup>OSHA – Occupational Safety and Health Administration.

<sup>2</sup>PEL – permissible exposure limit as an 8-hour time-weighted average (TWA) concentration.

<sup>3</sup>CEIL – ceiling limit, absolute exposure limit that should not be exceeded at any time ppm-part per million.

<sup>4</sup>NIOSH – National Institute for Occupational Safety and Health.

<sup>5</sup>REL – recommended exposure limit (REL) as an 8-hour TWA. The limit is based on the risk of cardiovascular effects.

<sup>6</sup>ACGIH – American Conference of Governmental Industrial Hygienist.

<sup>7</sup>TLV – threshold limit value as a TWA for a normal 8-hour workday and a 40-hour workweek. The limit is based on the risk of elevated carboxyhaemoglobin levels.

**Table 4:**

Acute effects of carbon monoxide [41].

Concentration	Symptoms
31 mg/kg (40 mg/m <sup>3</sup> ; 35 ppm or 0.0035%)	Headache and dizziness within six to eight hours of constant exposure.
89 mg/kg (115 mg/m <sup>3</sup> ; 100 ppm or 0.01%)	Slight headache in two to three hours.
177 mg/kg (229 mg/m <sup>3</sup> ; 200 ppm or 0.02%)	Slight headache within two to three hours; loss of judgment.
354 mg/kg (458 mg/m <sup>3</sup> ; 400 ppm or 0.04%)	Frontal headache within one to two hours.
708 mg/kg (916 mg/m <sup>3</sup> ; 800 ppm or 0.08%)	Dizziness, nausea, and convulsions within 45 min; insensible within 2 hours.
1,417 mg/kg (1,832 mg/m <sup>3</sup> ; 1,600 ppm or 0.16%)	Headache, tachycardia, dizziness, and nausea within 20 min; death in less than 2 hours.
2,835 mg/kg (3,665 mg/m <sup>3</sup> ; 3,200 ppm; 0.32%)	Headache, dizziness and nausea in five to ten minutes. Death within 30 minutes.
5,668 mg/kg (7,329 mg/m <sup>3</sup> ; 6,400 ppm or 0.64%)	Headache and dizziness in one to two minutes. Convulsions, respiratory arrest, and death in less than 20 minutes.
11,337 mg/kg (14,659 mg/m <sup>3</sup> ; 12,800 ppm or 1.28%)	Unconsciousness after 2-3 breaths. Death in less than three minutes.

**Table 5:**

Occupational exposure limits for carbon dioxide [42,43,46,47].

Occupational exposure standards	Exposure limits
U.S. EPA <sup>1</sup>	Max=1,392 mg/kg (1800 mg/m <sup>3</sup> ; 1000 ppm or 0.1%) for continuous exposure
ASHRAE standard 62-1989 <sup>2</sup>	Max=1,392 mg/kg (1800 mg/m <sup>3</sup> ; 1000 ppm)
NIOSH REL (United States, 6/2001) <sup>3-6</sup>	STEL: 54000 mg/m <sup>3</sup> 15 minute(s) STEL: 41,763 mg/kg (30000 ppm) 15 minute(s) TWA: 9000 mg/m <sup>3</sup> 10 hour(s) TWA: 6,961 mg/kg (5000 ppm) 10 hour(s)
OSHA PEL (United States, 1993) <sup>5,7,8</sup>	TWA: 9000 mg/m <sup>3</sup> 8 hour(s). TWA: 6,961 mg/kg (5000 ppm) 8 hour(s).
ACGIH TLV (United States, 9/2004) <sup>5,6,9,10</sup>	STEL: 54000 mg/m <sup>3</sup> 15 minute(s) STEL: 41,763 mg/kg (30000 ppm) 15 minute(s) TWA: 9000 mg/m <sup>3</sup> 8 hour(s) TWA: 6,961 mg/kg (5000 ppm) 8 hour(s)

<sup>1</sup>U.S. EPA – U.S. Environmental protection Agency.<sup>2</sup>ASHRAE – American Society of Heating, Refrigerating and Air-Conditioning Engineers.<sup>3</sup>NIOSH – National Institute for Occupational Safety and Health. The limit is based on the risk of cardiovascular effects.<sup>4</sup>REL – recommended exposure limit (REL) as an 8-hour TWA.<sup>5</sup>STEL – average for a short-term (15 minute) exposure limits.<sup>6</sup>TWA – time-weighted average concentration.<sup>7</sup>OSHA – Occupational Safety and Health Administration.<sup>8</sup>PEL – permissible exposure limit as an 8-hour time-weighted average (TWA) concentration.<sup>9</sup>ACGIH – American Conference of Governmental Industrial Hygienist. The limit is based on the risk of elevated carboxyhemoglobin levels.<sup>10</sup>TLV – threshold limit value as a TWA for a normal 8-hour workday and a 40-hour workweek.

ppm – part per million.

tion to ambient concentration in parts per million and the portion in % are listed in the **Table 6** [47].

Another combustion product is hydrogen chloride. It is colourless to slightly yellow compressed liquefied gas, with pungent odour and heavier than air. It readily dissolves in water to form hydrochloric acid, a corrosive solution ( $\text{HCl} + \text{H}_2\text{O} \rightarrow (\text{H}_3\text{O})^+ + \text{Cl}^-$ ). Hydrogen chloride exposure levels and associated health impacts in acute exposure situations are presented in the **Table 7** [48]. Chronic exposure to low levels may affect tooth enamel, cause corrosion, coughing, shortness of breath, bronchitis. It may also cause respiratory cancers and may affect the liver and kidneys.

During combustion of PVC materials a high amount of hydrogen chloride is produced. It may cause severe chemical burns in respiratory tract. Hydrogen chloride binds on small parts of carbon, which are inhaled and transported to the alveolus.

**Table 6:**  
Acute effects of carbon dioxide [47].

Concentration	Effects
13,918 mg/kg (17,996 mg/m <sup>3</sup> 10,000 ppm or 1%)	Breathing rate increases slightly.
27,836 mg/kg (35,992 mg/m <sup>3</sup> 20,000 ppm or 2%)	Breathing rate increases to 50% above normal level. Prolonged exposure can cause headache, tiredness.
41,754 mg/kg (53,988 mg/m <sup>3</sup> 30,000 ppm or 3%)	Breathing increases to twice normal rate and becomes labored. Weak narcotic effect. Impaired hearing, headache, increased blood pressure and pulse rate.
55,672- 69,590 mg/kg (71,984-89,980 mg/m <sup>3</sup> 40,000-50,000 ppm or 4-5%)	Breathing increases to approximately four times normal rate, symptoms of intoxication become evident, and slight choking may be felt.
69,590-139,179 mg/kg (89,980-179,959 mg/m <sup>3</sup> 50,000-100,000 ppm or 5-10%)	Characteristic sharp odour noticeable. Very labored breathing, headache, visual impairment, and ringing in the ears. Judgment may be impaired, followed within minutes by loss of consciousness.
139,179-1391,795 mg/kg (179,959-1799,591 mg/m <sup>3</sup> 100,000-1000,000 ppm or 10-100%)	Unconsciousness occurs more rapidly above 10% level. Prolonged exposure to high concentrations may eventually result in death from asphyxiation.

**Table 7:**  
Hydrogen chloride exposure levels and associated health impacts in acute exposure (<15 minutes) situations [48].

Concentration	Health impacts
0.29-11.6 mg/kg (0.37-15 mg/m <sup>3</sup> or 0.25-10 ppm)	Readily detectable odour. Eye, nose, and throat irritation, corrosive, burning sensation. Liquid exposure to skin or eyes will cause frostbite, serious skin burns, corrosion, pain, and blurred vision or blindness. Ingestion will cause nausea, vomiting, and intense thirst. Symptoms may be delayed.
>11.6 mg/kg (>15 mg/m <sup>3</sup> or >10 ppm)	Corrosive skin burns, sneezing, laryngitis, hoarseness, chest pain feeling of suffocation.
58 mg/kg (75 mg/m <sup>3</sup> or 50 ppm)	Immediately dangerous to life and health.
>58 mg/kg (>75 mg/m <sup>3</sup> or >50 ppm)	Pulmonary edema, laryngeal spas. Ingestion will cause esopharangeal burns, gastric perforation, and peritonitis. Note: The symptoms often do not manifest until after a few hours and physical exertion will aggravate this condition. Rest and medical observation are essential.



PVC presents serious problem in fire fighting today because it releases hydrogen chloride gas and other combustion products when burning. Inhalation of PVC combustion products leads to several respiratory symptoms including slow and shallow breathing, cough, hoarseness, chest pain, shortness of breath and wheezing. Dyer and Esch [49] from 1970 to 1975 studied one hundred seventy fire fighters who experienced symptoms from its toxicity. One died. Chemical Safety Board [50] found that a massive release of vinyl chloride led to the explosion that killed 5 workers at a PVC factory in Illiopolis, Illinois on April 23, 2004.

Lestari et al. [51] investigated an in vitro cytotoxicity of combustion products of PVC and other polymers (polyethylene, polypropylene, polycarbonate, fibreglass reinforced polymer, and melamine-faced plywood) on human lung cells. Results indicated that PVC (IC<sub>50</sub>, 50% inhibitory concentration: 1.2 mg/L) was the most toxic of the materials tested followed by polyethylene, polypropylene, fibreglass reinforced polymer, polycarbonate and melamine-faced plywood.

During PVC combustion also dioxins are produced. However, dioxins are created in the whole life cycle of PVC materials (i.e. production, recycling, disposal, and incineration). Dioxins are of concern because of their highly toxic potential. The characteristic adverse effect following a severe acute exposure to dioxins is chloracne, the onset of which may be delayed several months. Acute exposure to dioxins may also cause nausea, vomiting, diarrhoea, hepatic damage and neurological effects. The adverse effects of chronic exposure to dioxins are similar to those following acute exposure. Dioxins are readily absorbed by ingestion and are also likely to be absorbed by inhalation or dermal exposure. Once absorbed, they are extensively distributed throughout the body, with particular accumulation in the liver and adipose tissue. The metabolism of dioxins is extremely slow, with partial excretion in the faeces as metabolites. They are extremely persistent with the elimination half-life of 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) being 7 to 12 years; therefore, there is potential for accumulation in body tissues. Chronic exposure to dioxins may also cause liver disease, increased risk of developing diabetes, alterations in thyroid function, impaired immune function, cardiovascular disease, mild neuropathies and developmental effects. TCDD is classified by International Agency for Research on Cancer (IARC) as being carcinogenic to humans [52,53].

According to the risk of dioxin emissions during the whole life cycle of PVC products, Technical and Scientific Advisory Committee of the US Green Building Council [54] released a report on a PVC avoidance related materials credit for the LEED Green Building Rating system. The report concludes that “no single material shows up as the best across all the human health and environmental impact categories, nor as the worst” but that the “risk of dioxin emissions puts PVC consistently among the worst materials for human health impacts” [54]. Besides the mentioned combustion products, serious hazards produced in fires are also smoke and soot. Smoke can drastically reduce visibility and has

Results indicated that PVC (IC<sub>50</sub>, 50% inhibitory concentration: 1.2 mg/L) was the most toxic of the materials tested followed by polyethylene, polypropylene, fibreglass reinforced polymer, polycarbonate and melamine-faced plywood.

The literature review showed that the field of health concerns of PVC building materials in case of fire is not thoroughly investigated.

unpleasant physiological effects. A major component of smoke from flames is soot. Soot refers to impure carbon particles resulting from the incomplete combustion of hydrocarbon. Soot is the major factor that affects the visibility. As airborne particulate matter it is considered hazardous to the lungs and general health when the particles are less than five micrometers in diameter, as such particles are not filtered out by the upper respiratory tract [55].

The literature review showed that the field of health concerns of PVC building materials in case of fire is not thoroughly investigated. There exist some reports on actual events of PVC burning and their negative consequences on the health of fire fighters. However, studies on health concerns of PVC materials in buildings in case of fire are rare. Therefore, here are presented the results of the study by Senica [56] (the study was executed under mentorship, counselling of Kristl and Dovjak). Senica [56] conducted comparative study of various fire scenarios in an actual storage building for PVC products in Slovenia. The calculations were executed with Nist Fire Dynamic Simulator (FDS) 5.5.1 and presented with Smokeview (SMW) 5.5.6 [57]. FDS is a computational fluid dynamics (CFD) model of fire-driven fluid flow. The software solves numerically a form of the Navier-Stokes equations appropriate for low-speed, thermally-driven flow, with the emphasis on smoke and heat transport from fires. SMV is a visualization program that is used to display the output of FDS [57]. The dimensions of the building are 24.2 m/9.2 m. In the building there is the storage for PVC products (130 m<sup>2</sup>), an office and a depository. In the storage there are seven metal racks (4.0 m long, 1.20 m wide and 2.50 m high). The stored material is PVC sewage and drainage pipes. The overall quantity of stored PVC amounts to 2.64 m<sup>3</sup>. The simulation focused on two neighbouring spaces, the storage for PVC products and the office connected with a door.

Three fire scenarios were simulated:

- Uncontrolled spread of fire in the storage with open doors and windows presented state-of-art (V1).
- Limited spread of fire with mounted heat detectors and sprinklers, the doors and windows left open (V2).
- Controlled spread of fire with closed doors and windows, the door between the storage and the office is left open (V3).

During the simulations fire dynamics (fire growth and fire spread), surface temperatures, air temperatures, smoke dynamics and concentration of combustion products (CO, CO<sub>2</sub>, O<sub>2</sub>, soot) were observed. Hydrogen chloride and dioxins were not taken into consideration, because FDS calculation program enables observation just for selected combustion products (i.e. CO, CO<sub>2</sub>, O<sub>2</sub>, and soot). Although all the PVC combustion products were not simulated in the study, one can get interesting information about negative health effects of the burning PVC products. In all three scenarios the fire started at the same location in the middle of the storage near the rack. As expected, in V1 the fire quickly spreads on the racks with stored PVC products (after 70 s the

first rack is burning, after 150 s the fire spreads to the neighbouring racks). The fire also spreads into the office. After 330 s (when the majority of the material has burnt down) the fire gradually diminishes but does not cease completely until 830 s. As seen in this scenario, the highly flammable composition of the material and large supply of oxygen result in fire accelerating out of control in a fairly short time after the flashover. After 130 s in the storage there is near-zero visibility and after 270 s both spaces are completely filled with smoke; the amount of smoke does not diminish until the end of the simulation in the 900<sup>th</sup> sec. Due to intensive burning of the stored material the concentration of CO is the highest between 200 sec and 300 sec of the simulation, when the concentration reaches 132,853 mg/kg (150,000 ppm or 171,779 mg/m<sup>3</sup>). Later the concentration diminishes to 17,714 mg/kg (22,904 mg/m<sup>3</sup> or 20,000 ppm), but the value is still high and life threatening. According to OSHRAE [41]; 11,337 mg/kg (14,659 mg/m<sup>3</sup>; 12,800 ppm or 1.28 %) causes unconsciousness after 2-3 breaths and death in less than three minutes (**Table 5**). The concentration of CO does not diminish to less than 10,628 mg/kg (13,742 mg/m<sup>3</sup> or 12,000 ppm) until 430 s of the fire simulation.

In the office the concentration of CO is lower (the maximum concentration of CO is reached after 365 s and amounts to 12,400 mg/kg (16,033 mg/m<sup>3</sup> or 14,000 ppm), the average concentration during the fire is 5,314 mg/kg (6,871 mg/m<sup>3</sup> or 6,000 ppm). Concentration of 5,668 mg/kg (7,329 mg/m<sup>3</sup>; 6,400 ppm or 0.64 %) causes headache and dizziness in one to two minutes, convulsions, respiratory arrest, and death in less than 20 minutes (Table 5) [41]. Besides high concentration of CO, CO<sub>2</sub> also reaches high levels. After 220-300 s the CO<sub>2</sub> concentration is 417,539-556,718 mg/kg (539,877-719,836 mg/m<sup>3</sup> or 300,000-400,000 ppm). According to OSHA [47] at 139,180-1,391,795 mg/kg (179,959-1,799,591 mg/m<sup>3</sup>; 100,000-1,000,000 ppm or 10-100%) CO<sub>2</sub> there occurs rapidly unconsciousness and prolonged exposure to high concentrations results in death from asphyxiation. The second consequence of intensive combustion of the stored material is high amount of the released heat that results in temperatures reaching 1.600 °C – 1.800 °C at the measuring points after 210 s and 240 s, respectively. The average temperature is 400 °C. Bearing in mind that the temperature that normally causes skin burn is 60 °C a person caught near the fire (standing at the measuring points) would suffer burns after 35 s in the storage and after 90 s in the office. The state-of-art simulation showed that the temperatures and combustion products would cause death after one to two minutes if a person would not evacuate immediately or if intervention team would enter unprotected.

The V2 simulated scenario with open windows and doors and with sprinklers activated at a temperature of 80 °C. The sprinklers prevented the temperatures from exceeding 100 °C (except for a short time between 250 s and 255 s) in the storage. The average temperature in the storage was 60 °C and in the office 26 °C (max. 36 °C in the 125<sup>th</sup> s). The fire was kept under control. The amount of combustion product

gases was kept low (and ventilated into the external air). The concentration of CO<sub>2</sub> in the storage reached the maximum value of 173,974 mg/kg (224,949 mg/m<sup>3</sup> or 12,500 ppm) and average value of 13,918 mg/kg (17,996 mg/m<sup>3</sup> or 10,000 ppm). At 13,918 mg/kg (17,996 mg/m<sup>3</sup>; 10,000 ppm or 1 %) the breathing rate increases slightly [47]. The maximum value of 4,871 mg/kg (6,299 mg/m<sup>3</sup> or 3,500 ppm) in the office was reached during the time span from 600 s to 620 s and would not cause harmful effects during acute exposure. The average concentration of CO in the office was 177 mg/kg (229 mg/m<sup>3</sup> or 200 ppm), which causes slightly headache and loss of judgement in exposed persons [41]. In the storage the concentration was kept at about 797 mg/kg (1,031 mg/m<sup>3</sup> or 900 ppm) and did not exceed 974 mg/kg (1,260 mg/m<sup>3</sup> or 1,100 ppm). CO concentration of 709 mg/kg (916 mg/m<sup>3</sup> or 800 ppm) may cause dizziness, nausea, and convulsions if a person would not evacuate immediately [41]. Fire did not spread into the office.

In V3 the scenario with closed windows and doors was simulated. The calculation showed that the burning rate was slower due to prevented air inflow. At the beginning of the fire the amount of oxygen was still high. The temperature increased rapidly and at the measuring points it exceeded 100 °C after 75 s in the storage and after 77 s in the office. The maximum temperature in the storage reached 350 °C and stabilised at 400 °C – 500 °C after 350 s. The maximum temperature in the office was 250 °C. A person caught in the building would suffer burns after 20 s in the storage and after 50 s in the office. The smoke filled both spaces very quickly. The concentration of CO constantly increases up to 4,384 mg/kg (5,669 mg/m<sup>3</sup> or 4,950 ppm) in the 900<sup>th</sup> s. The CO<sub>2</sub> concentration reached 31,733 mg/kg (41,031 mg/m<sup>3</sup> or 22,800 ppm) after 200 s. This variant showed higher concentrations of CO and CO<sub>2</sub> at the beginning of the fire (between 0 and 200 s) than the remaining two variants. The concentration stabilised after 300 s (the supply of oxygen was gradually exhausted and the fire diminished).

The comparison shows that the most favourable variant was V2 with heat detectors and sprinklers that limited the fire to the first rack and did not allow spread of fire to the rest of the stored material. As a consequence, the amount of smoke and other combustion products as well as temperatures were lower than in the other described variants. Lower concentrations of combustion products as well as lower temperatures would enable safer evacuation of people than in other variants. Moreover, the occupational exposure limits for CO and CO<sub>2</sub> [42] were not exceeded. The same conclusions were made by Yimin et al. [58]. Yimin et al. [58] showed that low pressure water mist has a strong effect on the suppression of PVC fire as well as on the reduced monoxide and smoke concentrations. The less favourable situation was V1. In the storage CO reached the maximal concentration 132,853 mg/kg between 200 s and 300 s. The maximal concentration of CO was 11,337 mg/kg (14,659 mg/m<sup>3</sup>; 12,800 ppm or 1.28%) and exceeded lethal concentration by 12 times [41,42]. During that time the maximal concentration of CO<sub>2</sub> was 695,898 mg/kg. The concentration of CO<sub>2</sub> reached the le-

Yimin et al. showed that low pressure water mist has a strong effect on the suppression of PVC fire as well as on the reduced monoxide and smoke concentrations.

thal concentration of 139,179-1.391,795 mg/kg (179,959-1.799,591 mg/m<sup>3</sup> 100,000-1.000,000 ppm or 10-100%) in 200 s [47]. In V3, the concentration of CO was 30 times lower than concentration in V1, and concentration of CO<sub>2</sub> was 22 times lower than concentration in V1.

#### 4. DISCUSSION

EU and Slovenian legislations in the field of PVC materials in the built environment are partial and ill-defined. The same phthalates are used for the production of toys, childcare articles, cosmetics, food contact applications, medical equipment and building materials. Nevertheless, the restrictions on use of PVC materials in the above mentioned products strongly vary:

- DEHP is not permitted for use in the EU in toys and childcare articles or in cosmetics and is subject to certain restrictions in food contact applications. As with all chemical substances, DEHP will have to be registered for use in Europe under the new EU Chemicals legislation REACH [59]. It will also have to eventually undergo authorisation, although this is expected to be granted for its current applications on the basis that its use is adequately controlled [60].
- The European Commission has confirmed that diisodecyl phthalate (DIDP) poses no risk to either human health or the environment from any current use [61].
- In Europe DINP can no longer be used in toys and childcare items that can be put in the mouth, even though the EU scientific risk assessment concluded that its use in toys does not pose a risk to human health or the environment [27].
- The risk assessment conclusions clearly state that there is no need for any further measures to regulate the use of DBP in finished products [62].
- The risk assessment conclusions clearly state that there is presently no need for further information and/or testing of BBP [63].

On the basis of the review of building standards carried out by Senica [56] it can be concluded that there exist no restrictions concerning the chemical composition for PVC construction products. Methods and procedures of measurements for selected phthalates are defined but no declaration of chemical composition of the materials is required. It is interesting that EU repudiates the harmful effect of phthalates that were proven with studies, but on the other side new regulations on restrictions for their marketing and use are adopted, especially for childcare products [64].

The above cited studies on children and adults exposed to PVC building products show positive association between exposure to phthalates and appearance of asthma and allergies (odds ratio 1.20 - 2.50, 95 % confidence interval). An odds ratio of 1 implies that the appearance of symptoms/illness in a group exposed to hazard is equal to the appearance in unexposed group. An odds ratio greater than one implies that

The same phthalates are used for the production of toys, childcare articles, cosmetics, food contact applications, medical equipment and building materials.

In Germany and Austria, a number of towns and cities have decided not to use PVC materials for new public buildings.

that the appearance of symptoms/illness is more likely in the exposed group [20]. Acute exposure (i.e. short-term exposure) may result in mild skin reactions, such as eczema, blush, as well as difficulty in breathing and wheezing. Chronic exposure (i.e. long-term exposure) may cause bronchial obstruction, asthma, skin irritation, mucosa irritation, and respiratory tract irritation. Phthalates are dermal and respiratory irritants that can disrupt the proper functioning of the body's endocrine system and lead to structural abnormalities in the reproductive systems, especially of male population. Moreover, basic raw materials for PVC production are oil and chlorine-with proven carcinogenic effects.

Coadogan [22] argues that despite the scientific facts that have proven the negative impact of PVC materials on human health, ECPI [21] believes that it is now generally agreed that the carcinogenic effects produced by phthalates in rodents are species-specific and of no relevance to humans. In addition, there is no evidence that phthalates produce hormone-like effects at low dose levels that could cause reproductive problems in humans. ECPI asserts that the on-going risk assessments will only be credible and result in appropriate risk reduction strategies if the studies used to define the reproductive endpoints are chosen on their scientific merit rather than on political or precautionary. Phthalates labelled with the skull and crossbones symbol may still be used safely in the workplace. Moreover, European Commission concluded that there is no need for further measures to regulate phthalates [27,62-64]. It should be pointed out that the second largest consumer of PVC is building industry; phthalates are present in 50 % of the overall production of PVC. Improvements have been made in the field of toys and food contact applications. It is necessary to restrict phthalates especially in the construction products that are in contact with children. They present a sensitive group with higher risks (quicker accumulation due to lower body weight, higher activity levels and higher intake due to age-related behavioural characteristics).

Despite the fact that ECPI [21] classifies phthalate plasticizers as non-carcinogenic, there exists public concern that chlorinated organics may cause cancer in adults and adverse health and reproductive effects in the offspring of both humans and wildlife. It has already brought regulations and the banning of selected products as well as calls from several groups for an eventual phase out of at least some sectors of the chlorine industry [65]. In Germany and Austria, a number of towns and cities have decided not to use PVC materials for new public buildings. Four of the nine regional capitals in Austria (Vienna, Linz, Salzburg, and Innsbruck) have PVC-free construction policies for public buildings, and two Austrian states have followed suit. More than 100 German communities will no longer use PVC in their new public buildings [66]. A trend to convert to PVC- and DEHP-free products is going on also in hospitals and medical institutions [67].

In the years since, because of public pressure from environmental health groups, shareholder resolutions to major manufacturers and, most significantly, hospital demand, the market has been shifting toward safer alternatives. A major breakthrough in safer materials was

announced at CleanMed 2006, when Hospira Inc., became the first leading hospital supplier to launch a full-service, PVC-free, DEHP-free IV container [68]. At CleanMed 2006, Health Care Without Harm also announced a list of more than 100 healthcare organizations that have undertaken efforts to reduce PVC and/or DEHP, including six of the largest group purchasing organizations (GPOs) and some of the leading healthcare systems and hospitals in the country. Vinyl wall guards are being replaced by polycarbonate/ABS blends and polyethylene. Vinyl window treatments are being replaced by polyethylene and polyester. Furniture manufacturers are getting the last PVC out of their products. PVC carpet backings are being replaced by polyolefins, polyurethane, and recycled polyvinyl butyral. Vinyl floors are being replaced by rubber and polyolefins, as well as by the return of the classic linoleum. Replacement of PVC products with safer alternatives has benefits for patient and staff safety and caregiver efficacy, as well as increased environmental responsibility [68].

Against all expectations and against the advice of the government, on May 3<sup>rd</sup> 2011 the French National Assembly (lower house of parliament) passed the first reading of the bill proposed by Yvan Lachaud which seeks to ban the use of phthalates, parabens and alkylphenols. The outcome of the vote has provoked a number of reactions and articles in the media. Some of these articles have implied a change in the regulations and as a result an immediate ban on the substances mentioned above. However, this bill has not yet been passed by the parliament and thus has not come into force. The first reading in the National Assembly is the first step in the ongoing decision-making process. This bill has been presented to the Senate (the upper house) for debate, which is likely to take place in the next couple of months [69].

## 5. CONCLUSIONS

PVC use in relation to building materials and health issues is not referenced in the legislation of the Republic of Slovenia, or in that of the European Union. First incentives on the local level have already been implemented, which points out the increasing awareness of the public regarding the PVC health impacts. Adoption and implementation of regulations and standards on the marketing and use of phthalates in building materials are the next probable step towards healthier indoor environment. The literature review on health concerns associated with phthalate exposure in everyday life let us conclude that phthalates have adverse health effects. Most exposed population is young children and certain groups of adults during occupational exposure. Various studies have indicated that these chemicals may be endocrine disruptors and may lead to the development of asthma, allergies, or related respiratory effects. These findings underline the need to consider the health aspects of materials used for constructional complexes. Regarding the conclusions of the reviewed studies, the recommendations for prevention of negative health effects of PVC materials are systematically unfolded. They include the actions regarding the whole life cycle of PVC

Various studies have indicated that these chemicals may be endocrine disruptors and may lead to the development of asthma, allergies, or related respiratory effects.

**Table 8:**  
List of recommendations.

Level of control	Recommendation
<b>Legislation</b>	<ul style="list-style-type: none"> <li>• Adoption and implementation of national and international regulations and standards especially on PVC restrictions in construction products.</li> <li>• Restrictions concerning the chemical composition of used PVC materials for construction products.</li> <li>• Definition of methods and procedures of measurements for phthalates in construction products.</li> </ul>
<b>Production</b>	<ul style="list-style-type: none"> <li>• Change of toxic chemicals (plastificators-phthalates, stabilisators-organic compounds based on lead, zinc, barium, or cadmium; substances that reduce the rate of burning-chlorinated paraffin) with safer alternatives (i.e. production of PVC-free, phthalate-free, DEHP-free products, etc.).</li> <li>• Production of biodegradable plastic materials.</li> </ul>
<b>Use</b>  <b>Normal use</b>  <b>Extraordinary circumstances</b>	<ul style="list-style-type: none"> <li>• Use of healthy and environment friendly building materials.</li> <li>• Use of safer alternatives: i.e. PE foil instead of PVC foil; bamboo, wood, stone, cork; linoleum flooring, ceramic tile, glass tile, rubber carpets instead of PVC flooring or wall to wall carpets; wooden window frames instead of PVC frames; bituminous tape, polyethylene tape, polypropylene plate, glass plate or ceramic tiles instead of PVC tape. Alternative to PVC pipes are ductile stainless thin pipes, concrete pipes or polyethylene pipes.</li> <li>• Compliance with basic requirements of EU Regulation EU 305/2011 [70] on harmonized conditions for the marketing of construction products: Safety in case of fire; Hygiene, health and the environment; Sustainable use of natural resources.</li> <li>• Life cycle analysis (LCA) has to be carried out.</li> </ul>
<b>Waste management strategy</b>	<p>Waste management strategy includes hierarchical actions (1-5):</p> <ol style="list-style-type: none"> <li>1. Prevention (avoidance), minimization, and reuse of PVC waste materials <ul style="list-style-type: none"> <li>• An important method of waste management is the prevention of PVC waste material being created.</li> <li>• Methods of avoidance include reuse of second-hand PVC products and designing products that use less material to achieve the same purpose.</li> </ul> </li> <li>2. Recycling <ul style="list-style-type: none"> <li>• Recycled plastic from plastic cans can be used for plastic pipes.</li> </ul> </li> <li>3. Incineration <ul style="list-style-type: none"> <li>• Control of combustion products (dioxins) and water leakage polluted with heavy metals (chlorine, lead, cadmium).</li> </ul> </li> <li>4. Waste treatment <ul style="list-style-type: none"> <li>• Dechlorination of Cl component must be removed from any waste PVC.</li> </ul> </li> <li>5. Final disposal <ul style="list-style-type: none"> <li>• Management of waste water leakages (soil and water contamination with phthalates, heavy metals)</li> <li>• Fire prevention.</li> </ul> </li> </ol>

material with the emphasis on the use of PVC materials in buildings during their product use phase (**Table 8**).

The overview of studies on the use of PVC materials in case of fire shows that PVC presents serious problem because of high burn rate that results in high temperatures, dense soot, and other toxic combustion products such as hydrogen chloride gas. The results of Senica [56] show that CO and CO<sub>2</sub> rapidly reach life threatening concentrations. Storage of PVC materials requires high level of safety measures. It can be assumed that similar effect may be detected in case of fire in buildings, especially if PVC material is used in large quantities and as covering material.

Adverse effects related with use of PVC materials can be also detected in other phases of PVC life cycle (**Table 8**). For example the recycled



waste plastic is used for new products, where the composition remains more or less the same (i.e. recycled PVC used for plastic pipes). Moreover, every uncontrolled phase of waste management may be connected to environmental and health problems: i.e. uncontrolled final disposal and eventual fires result in release of toxic combustion products; uncontrolled waste water leakages lead to water pollution; uncontrolled incineration may result in air pollution.

Additional research, further measurements of phthalate release from building materials and health impacts are needed to achieve the uniform opinion about health risks of phthalates on human health. Research and development for searching new alternatives, non toxic chemicals for safer production, use of PVC free materials and improvements on the level of waste treatment are needed.

Research and development for searching new alternatives, non toxic chemicals for safer production, use of PVC free materials and improvements on the level of waste treatment are needed.

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# Pridobivanje klorovega dioksida za pripravo pitne vode

## The Generation of Chlorine Dioxide for drinking water treatment

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### POVZETEK

Poenotenje nacionalnih predpisov za pripravo vode zahteva uporabo evropskih normativov DIN EN 878 do DIN EN 14369. Za izdelavo klorovega dioksida za sanitarne namene DIN EN 12671 opisuje tri postopke po katerih lahko proizvedemo  $\text{ClO}_2$  kot vodno raztopino z ustrežno kvaliteto čistosti za obdelavo pitne vode. Za izdelavo raztopine klorovega dioksida s čim nižjo vsebnostjo neželenih produktov, je potrebno s klorovodikovo kislino/kloratom (III) oziroma klor/kloratom (III) proizvesti visoke koncentracije vmesnega produkta  $\text{Cl}_2\text{O}_2$ , ki pospeši reakcijo v  $\text{ClO}_2$  in  $\text{Cl}^-$ . Proizvodnja  $\text{ClO}_2$  z reakcijo med natrijevim peroksidisulfatom z natrijevim kloratom (III) vodi do stabilnejše vodne raztopine klorovega dioksida v pH nevtralni vodni raztopini.

### KLJUČNE BESEDE:

priprava vode, pitna voda, dezinfekcija, klorov dioksid.

### ABSTRACT

The standardization of the European national drinking water rules requires the common use of the European standards from DIN EN 878 to DIN EN 14369. In DIN EN 12671 the generation of chlorine dioxide for human application is described. There are three procedures for generating the pure chlorine dioxide solutions. For the generation of chlorine dioxide solutions which is poor in byproducts from the hydrochloric acid – chlorite procedure or from the chlorine – chlorite procedure there must be a high concentration of the intermediate  $\text{Cl}_2\text{O}_2$  to accelerate the reaction to  $\text{ClO}_2$  and  $\text{Cl}^-$ . The generation of chlorine dioxide by the reaction of sodium peroxodisulphate with sodium chlorite solutions results in more stable chlorine dioxide solutions in a pH-neutral milieu.

### KEY WORDS:

water treatment, drinking water, disinfection, chlorine dioxide.

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## 1. UVOD

S spremembo Predpisa o pripravi vode dne 5. 12. 1990 in s sprejetjem novega Predpisa za pripravo vode (TVO 2001) z dnem 28. 05. 2001, ki je stopil v veljavo 01. 01. 2003 v Zvezni republiki Nemčiji, je postala celotna vrsta predpisov "Produkti za pripravo vode za sanitarne namene" od DIN EN 878 do DIN EN 14369 osnova za kontrolo dovoljenih snovi glede na § 11 TVO 2001 [1].

Postopki in reaktanti za proizvodnjo klorovega dioksida za sanitarne namene so opisani v smernici DIN EN 12671. Kot reaktanti za proizvodnjo  $\text{ClO}_2$  so navedeni klor (EN 937), klorovodikova kislina (EN 939), natrijev klorat (EN 938), natrijev peroksidisulfat (EN 12926), natrijev klorat (I) (EN 901) in žveplova(VI) kislina (EN 899).

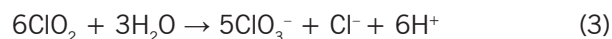
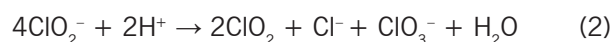
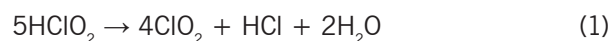
Naštete spojine uporabljamo v naslednjih postopkih za proizvodnjo klorovega dioksida:

1. Postopek s klorovodikovo kislino in kloratom (III).
2. Postopek s klorom in kloratom (III).
3. Postopek z natrijevim peroksidisulfatom in kloratom (III).
4. Postopek z žveplovo (VI) kislino, kloratom (I) in kloratom (III).

V nadaljevanju je predstavitev opisanih postopkov 1 – 4 po DIN EN 12671. Postopek 4 je modificiran klor/kloratni postopek. Za uporabo klorovega dioksida za pripravo pitne vode so za doseganje čiste raztopine klorovega dioksida postavljene zelo stroge zahteve pri kemičnih postopkih za proizvodnjo klorovega dioksida. Osnova za pravilen izbor naprav in postopkov za proizvodnjo klorovega dioksida je upoštevanje poteka in kinetike posameznih reakcij.

## 2. POSTOPEK S SOLNO KISLINO IN KLORATOM (I)

Za pridobivanje klorovega dioksida uporabimo 7,5 % raztopino natrijevega klorata in 9 % raztopino klorovodikove kisline [2]. Obe raztopini zmešamo v prostorninskem razmerju 1:1 in nastane vodna raztopina klorovega dioksida po naslednjih kemičnih reakcijah 1, 2 in 3.



Teoretično lahko po enačbi (1) proizvedemo, glede na klorat (III), 80 % klorovega dioksida. Vendar to velja samo v primeru, če imamo 1.000 % prebitok klorovodikove kisline [2]. Praktično poteka pridobivanje klorovega dioksida po tem postopku s prebitkom klorovodikove kisline od 200 % do 300 %. Glede na klorat (III) nastane 68 % klorovega dioksida in istočasno pride do povečanja koncentracije klorata (V) kot stranskega produkta po reakciji (2). Klorov dioksid v koncentrirani raztopini (15 g/L – 18 g/L  $\text{ClO}_2$ ) razpade po reakciji (3) delno v klorat (V) in klor-

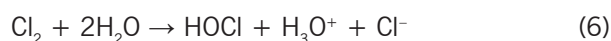
id. Zaradi teh reakcij koncentrirana raztopina klorovega dioksida hitro pade na koncentracijo 2 g/L–3 g/L  $\text{ClO}_2$  oziroma ga dodamo v vodo v želeni koncentraciji.

### 3. POSTOPEK S KLOROM IN KLOMATOM (V)

Pri tem postopku uporabimo klorovo (III) kislino ( $\text{HOCl}$ ) in tudi klor ( $\text{Cl}_2$ ). Obe spojini burno reagirata z raztopinami natrijevega klorata  $\text{NaClO}_2$ . Pri tem postopku iz plinastega klora in vode najprej nastane visoko koncentrirana kisl raztopina klora. Ta se zmeša v reaktorju z alkalno raztopino natrijevega klorata  $\text{NaClO}_2$ . Klor in klorat (III) reagirata po enačbah 4 in 5.



Ker so raztopine natrijevega klorata na trgu zaradi stabilnosti običajno dosegljive v alkalnem območju, raztopino stabiliziramo s presežkom klora. Klor reagira v vodi po enačbi 6.



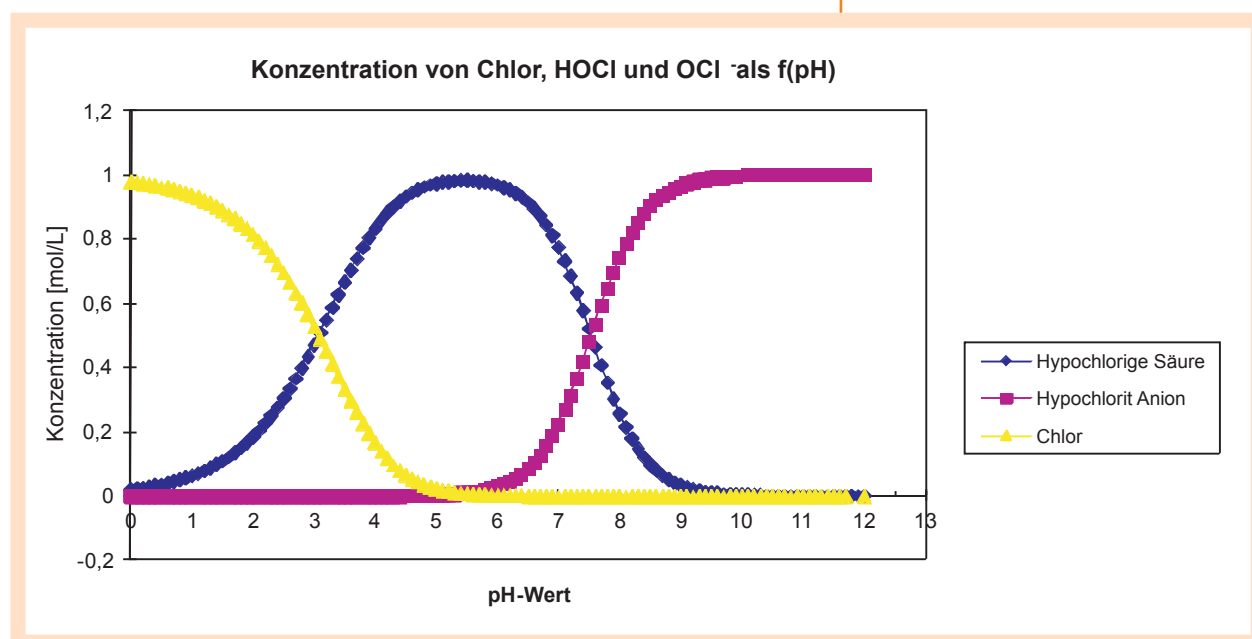
Zaradi tvorbe klorovodikove kisline se pH vrednost zniža, ker klorova (III) kislina in klor reagirata s kloratnimi (III) ioni.

Iz **slike 1** je razvidno, da je potrebno reakcijo voditi pod pH vrednostjo 6. Tvorba klorata pri reakciji med kloratom (III) in kloratom (I) pri pH vrednosti nad 6 poteka po enačbi 7 in vodi do povečanja koncentracije klorata (V) [3].

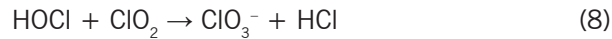


V praksi delamo s 30 % presežkom klora zaradi doseganja želenega kislega območja pH in doseganja tvorbe klorovega dioksida nad kon-

**Slika 1:** Koncentracija klora,  $\text{HOCl}$  in  $\text{OCl}^-$  kot funkcija pH vrednosti.



centracijo 97 %, glede na klorat (III) [2]. Previsoka koncentracija klora po enačbi 8 vodi do povišanega tvorjenja klorata (V) [4.1].



Pridobivanje klorovega dioksida po klor/kloratnem postopku dobimo iz treh reaktantov: natrijevega klorata (I), klorata (III) in in žveplove (VI) kisline (postopek A) in iz klora, klorata (III) ter kisline (postopek B).

### Postopek A

V alkalni raztopini natrijevega klorata (I) (NaOCl) in natrijevega klorata (III) z žveplove (VI) kislino nastavimo optimalno pH vrednost med 3,5 in 4. Alkalnosti (pogojeno z natrijevo lužino in natrijevim karbonatom) alkalnih reaktantov ne znižamo z uvajanjem plinastega klora v vodo in pretvorbo v klorovodikovo ter klorovo (I) kislino ampak z dodatkom žveplove (VI) kisline, tako da prebitek klora ni potreben. Stranske reakcije, kot npr. tvorbo kloratov na ta način preprečimo.

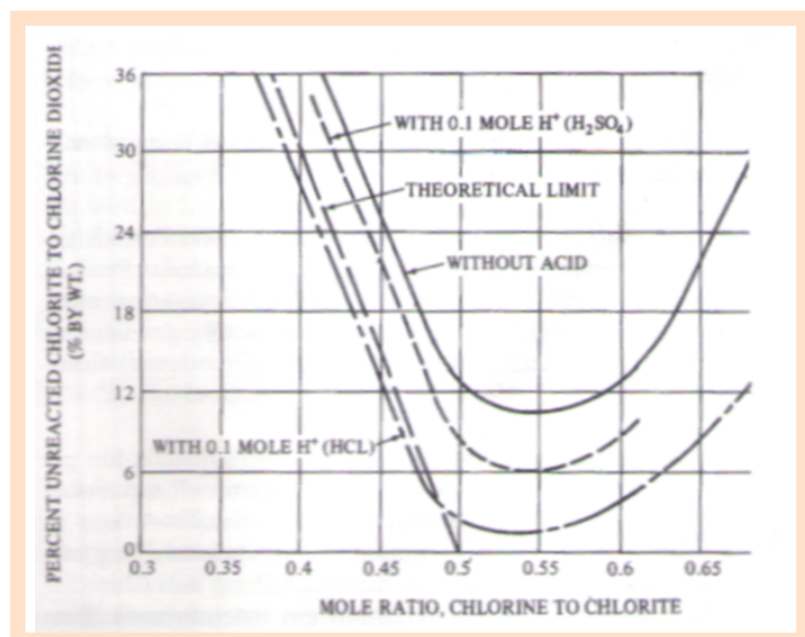
### Postopek B

Ta postopek je modifikacija postopka pridobivanja klorovega dioksida s klorom in kloratom (III). Pri kemični reakciji med klorom in kloratom (III) v reakcijsko raztopino dodamo majhno količino klorovodikove ali žveplove (VI) kisline. S tem znižamo prebitek klora za znižanje alkalnosti raztopine natrijevega klorata (III), ki vodi do povečane tvorbe klorata (V). Istočasno pri uporabi klorovodikove kisline reakcijski mešanici dodamo Cl katalizator že na začetku sinteze.

### Pridobivanje klorovega dioksida.

Vpliv katalizatorja na reakcijo je razviden iz **slike 2**. Reakcija alkalnih raztopin klorata (III) samo s plinastim klorom povzroči, da nad 10 % klorata (III) klor ne preide v klorov dioksid. Nastane klorat (V) kot stranski produkt. Zato dodamo žveplove (VI) kislino, zagotovimo minimalni

**Slika 2:**  
Tvorba klorovega dioksida glede na klorat (III) kot funkcija molarne razmerja klor – klorat (III) [4].

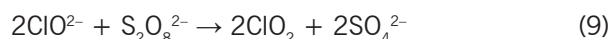




prebitek klorata za znižanje alkalnosti in zato se samo 6 % klorata (III) spremeni v klorat (V). Pri dodatku klorovodikove kisline praktično ne pride do stranske reakcije tvorbe kloratov (V) [4].

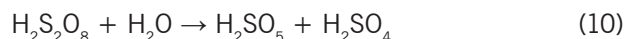
#### 4. PRIDOBIVANJE KLOROVEGA DIOKSIDA S PEROKSIDISULFATOM IN KlorATOM (III)

Po tem postopku se kloritni ion spremeni v klorov dioksid z peroksidisulfatom [5, 10] po enačbi 9.



Nastane čista raztopina klorovega dioksida, ki ne vsebuje klorata (III) in klorida ampak samo nizke koncentracije klorata (V). Reakcija mora potekati v pH območju v katerem so produkt klorov dioksid kot tudi reaktanta klorat (III) in peroksidisulfat stabilni, to je v pH območju med 5,5 in 8.

Pri pH območju nad 5,5 je koncentracija klorovega dioksida, klorata (V) in klorida nizka, ker je vsebnost klorove (III) kisline, (ki ima kislinsko vrednost 2), izredno nizka. Prav tako je reaktant natrijev peroksidisulfat v tem pH območju relativno stabilen. Pri nižjih pH vrednostih natrijev peroksidisulfat razpade v prosto peroksi (II) žveplovo kislino, kar vodi do hidrolize v peroksi (II) žveplovo kislino in žveplovo (VI) kislino [7], kot kaže enačba 10.



Prav tako je produkt klorov dioksid v nevtralnem vodni raztopini zelo stabilen [8, 9], v alkalnem območju razpade po enačbi 11.



Pri pH vrednostih pod 8, težnja k razpadu klorovega dioksida ni prisotna [6]. Če je reakcijska raztopina v pH območju, kjer sta reaktant (klorat (III)) kakor tudi produkt (klorov dioksid) stabilna, poteka oksidacija brez motečih stranskih produktov (razpad klorata (III) in klorovega dioksida).

Reakcija kloratnega (III) iona z ionom peroksidisulfata po enačbi 9 je zelo počasna, ker je korak, ki določa hitrost reakcije – razpad iona peroksidisulfata v dva  $\text{SO}_4^-$  radikala pri sobni temperaturi zelo počasna. Zaradi tega je proizvodnja vodne raztopine klorovega dioksida po tem postopku šaržna. Spontana tvorba klorovega dioksida ni možna. Do eksplozijske meje klorovega dioksida (6 g/L – 8 g/L  $\text{ClO}_2$ ) lahko proizvedemo poljubno koncentracijo klorovega dioksida. Zaradi zahtev varnosti pri delu je priporočena proizvodnja raztopin klorovega dioksida v koncentracijah pod 3 g/L. Po veljavni zakonodaji o varnem delu z nevarnimi snovmi do te koncentracije raztopine klorovega dioksida še ni potrebno deklarirati kot nevarno snov. Zato je ta postopek pridobivanja klorovega dioksida glede na zahteve o varnosti in zdravje pri delu neproblematičen [13]. V nasprotju s postopkoma s klorovodikovo kislino in kloratom (III) ter klorom in kloratom (III) je možno proizvajati čisto raztopino klorove-

ga dioksida iz nizko koncentrirane raztopine klorata (III). Koncentracije klorovega dioksida iz obeh omenjenih postopkov za pridobivanje klorovega dioksida v vmesnih stopnjah dosežejo koncentracije med 15 g/L in 20 g/L, medtem ko je koncentracija po postopku z natrijevim peroksidisulfatom vedno pod eksplozijsko mejo.

Za pridobivanje vodne raztopine po postopku s peroksidisulfatom in kloratom (III) zmešamo vodno alkalno raztopino klorata (III) s kislom raztopino natrijevega peroksidisulfata. Alkalni raztopini natrijevega klorata (III) primešamo puferno sredstvo (npr. binatrijev hidrogensulfat ali natrijev karbonat) za stabiliziranje pH vrednosti okrog vrednosti 7.

Pri šaržnem procesu vedno zmešamo določeno prostornino kloratne (III) raztopine z določeno koncentracijo klorata (III) skupaj z določeno količino natrijevega peroksidisulfata določene koncentracije. Natrijev peroksidisulfat zmešamo z določeno količino vode in jo kot vodno raztopino dodamo kloratni (III) raztopini.

Izkoristek procesa proizvodnje klorovega dioksida je skoraj 100 % glede na klorat (III) [10]. Koncentracija klorovega dioksida je po reakciji določena glede na vstopno koncentracije kloratnega (III) reaktanta. Mešanje obeh reaktantov mora opravljati usposobljeno osebje po navodilih proizvajalca. Če sta oba reaktanta popolnoma zmešana, nastane raztopina brez kloratov (III). Pri temperaturi 30 °C po 24 urah nastane raztopina klorovega dioksida in po tem času lahko klorov dioksid doziramo v zato predviden sistem.

Če uporabnik pridobiva klorov dioksid iz dvokomponentnega sistema, mora zagotoviti avtomatsko določevanje prehoda klorata (III) v klorov dioksid. Čas prehoda je možno meriti fotometrično pri valovni dolžini 360 nm. Fotometrični postopek je uporaben do meje detekcije 0,02 mmol/L klorovega dioksida, kar ustreza masni koncentraciji med 1 mg/L in 2 mg/L ClO<sub>2</sub> [8]. Ko dosežemo predpisano koncentracijo klorovega dioksida, naprava signal meritve posreduje krmilniku in ta lahko vklopi dozirno črpalko. Tako zagotovimo, da v pripravljene raztopine ni klorata (III).

Dolgoročna stabilnost po tem postopku pridobljenega klorovega dioksida je odvisna od temperature in skladiščenja (v temnih prostorih). Ugotovljeno je, da se v običajnih HD-PE posodah s koncentracijo 2,86 g/L klorovega dioksida v roku 30 dni njegova koncentracija zniža za 10,5 % in sicer na 2,56 g/L. Temperatura skladiščenja je v tem primeru znašala povprečno 5 °C. Tvorbe kloratov (III) ni bilo. Znižanje koncentracije klorovega dioksida je bilo 36 % zaradi difuzije plina skozi steno posode in oksidacije 35 % raztopine v klorat (V) (tvorba klorata (V) je bila omogočena s prebitkom natrijevega peroksidisulfata) in ker se je 29 % klorovega dioksida spremenilo v prosti klor [10].

Lastne raziskave avtorjev so pokazale, da se koncentracija klorovega dioksida v običajnih HD-PE posodah pri temperaturi 30 °C v roku 30 dni zniža iz 2,62 g/L na 1,69 g/L oz. za 35,5 %. Pri doziranju raztopin klorovega dioksida v pitno vodo do, v Nemčiji dovoljene koncentracije 0,2 mg/L klorovega dioksida po 30 dneh in pri temperaturi 5 °C kon-

centracija klorovega dioksida v vodi pade na 0,18 mg/L in pri temperaturi 30 °C celo na 0,13 mg/L.

Dezinfekcijo vodovodnih napeljav s klorovim dioksidom pridobljenim po postopku s peroksidisulfatom in kloratom (III) kljub vsemu lahko dosežemo v roku enega meseca. Glede na dokazano stabilnost je ta način pridobljene raztopine klorovega dioksida v času najmanj meseca dni za uporabo za dezinfekcijo pitne vode ustrezen, saj lahko raztopino po kontroliranju koncentracije, direktno uvajamo v sistem. Doziranje na ta način pridobljenega klorovega dioksida poteka po smernicah DVGW-Arbeitsblatt W624 [12].

## 5. KINETIKA KEMIČNIH REAKCIJ

Za zagotovitev čistih raztopin klorovega dioksida kot produkta za pripravo vode za sanitarne namene je nujno potrebno poznati reakcijske mehanizme in k temu spadajočo kinetiko kemičnih reakcij. Čiste raztopine naj bi vsebovale čim manj ionov klorata (III) in klorata (V) kakor tudi čim manj prostega klora. Kljub temu se v teh raztopinah tvorijo klorati (V) kot prikazuje enačba 8.

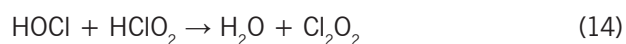
### 5.1 Postopek s (solno) kislino-kloratom (V)-in s klorom-kloratom (III)

Enačba 12 opisuje začetno reakcijo klorove (III) kisline ko niso prisotni kloridni ioni kot katalizator, npr. takrat ko poteka kisljenje raztopine z žveplovo (VI) kislino. Reakcija poteka v pH območju med 0,5 in 2 [14]. Enako velja za enačbo 13.

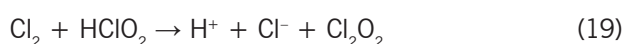
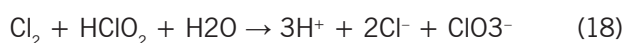
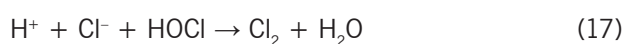
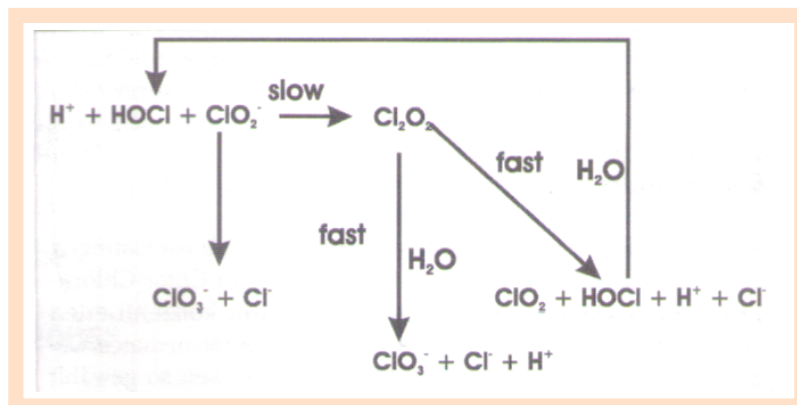


Po enačbah 12 in 13 nastala klorova (III) kislina reagira po enačbi 14 v vmesni produkt  $\text{Cl}_2\text{O}_2$  [9]. Ta vmesni produkt razpade po enačbi 15 v klorov dioksid in klor [15]. Ta razpad je odvisen od koncentracije vmesnega produkta  $\text{Cl}_2\text{O}_2$ . Klor reagira v koncentriranih raztopinah klorove (III) kisline po enačbi 19 v kloridne ione, ki delujejo kot katalizator v nadaljnjem poteku reakcije. V raztopinah z nizko koncentracijo klorove (III) kisline reagira klor s  $\text{HClO}_2$  in tvori klorate (V) po enačbi 18.

Enačbi 16 in 17 opisujeta tvorbo klora in kako klor v primeru dovolj visoke koncentracije klorove (III) kisline v raztopini reagira (enačbi 18 in 19). Iz tega je razvidno, da enačbe 16, 17, 18, 19 in 15 opisujejo postopek pridobivanja klorovega dioksida s klorovodikovo kislino in kloratom (III): medtem ko enačba 18 opisuje pot do povečanega tvorjenja kloratov (V) v nizko koncentriranih raztopinah. Enačbe 14, 19, 15 in kot katalizirana reakcija iz enačbe 17 opisujejo pridobivanje klorovega dioksida po postopku klor-klorat (III). Mehanizem reakcij je v obeh variantah poteka preko vmesnega produkta  $\text{Cl}_2\text{O}_2$ .



**Slika 3:**  
Mehanizem reakcije nastanka  
in razpada vmesnega produkta  
 $\text{Cl}_2\text{O}_2$  [16].



Vmesni produkt  $\text{Cl}-\text{ClO}_2$  se tvori samo, če reaktanti dosežejo dovolj visoko koncentracijo in sicer za kratek čas pri koncentracijah približno 100 g/L. Pri takšnih koncentracijah pride do samokondenzacije po enačbi 15 ali do reakcije s prisotnim kloratom (III) v klorov dioksid in klorid. Če med seboj reagirajo reaktanti v nizkih koncentracijah, pride do razpada slabo koncentriranega intermedijata  $\text{Cl}-\text{ClO}_2$  v klorat (III) in klorid (slika 3) [17].

## 5.2 Postopek peroksidisulfat-klorat (III)

Korak, ki je odločilen za hitrost reakcije po tem postopku je razpad peroksidisulfatnega iona in dveh  $\text{SO}_4^-$  radikalov po enačbi 20.



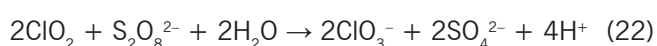
### Pridobivanje klorovega dioksida

Po tvorbi tega radikala kloratu (III) odvezamo elektron (enačba 21).

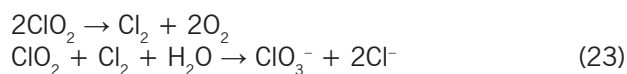


Za preprečevanje nastajanja prostega klora zaradi prisotnosti močnega oksidanta  $\text{SO}_4^-$ , ki lahko vodi do tvorbe klorata (V) s klorovim dioksidom, mora potekati reakcija v okolju, kjer ni kloridov.

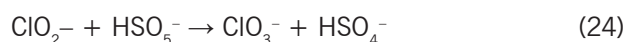
Za pospešitev postopka opisanega v enačbi 20 poteka reakcija s stehiometričnim prebitkom peroksidisulfatnega iona. Za pospešitev reakcije lahko reakcija poteka tudi pri višjih temperaturah. Upoštevati je potrebno tudi dejstvo, da lahko previsoka koncentracija peroksidisulfata vodi do oksidacije klorovega dioksida v klorat (V), kot opisuje enačba 22.



Prav tako lahko tudi višja temperatura zaradi termolize [8] po enačbi 23 vodi do razpada že nastalega klorovega dioksida.



Poleg tega mora potekati reakcija v pH nevtralnem območju zaradi preprečitve razpada peroksidisulfatnega iona v peroksomonosulfat in žveplove (VI) kisline, ker vodi reakcija peroksomonosulfata s kloratom (III) v klorat (V) [18].



## 6. ZAKLJUČEK

Pridobivanje čimbolj čiste raztopine klorovega dioksida po postopku klorovodikova kislina-klorat (III) in po postopku klor-klorat(III) zahteva uporabo koncentriranih reaktantov za doseganje visoke koncentracije vmesnega produkta  $\text{Cl}-\text{ClO}_2$ . Ta koncentracija mora biti taka, da v reaktorju ne dosegamo koncentracije klorovega dioksida pod 15 g/L in da ne presežemo koncentracije klorovega dioksida 20 g/L. Pridobivanja raztopin klorovega dioksida iz nizko koncentriranih mešanic klorat (III)-klorovodikova kislina ne uporabljamo zaradi prej omenjenih stranskih reakcij, ki vodijo do povečanja tvorbe klorata. pH področje nastavimo tako, da je  $\text{Cl}_2$  v presežku glede na  $\text{HOCl}$ .

Koncentrirane raztopine klorovega dioksida moramo (zaradi preprečevanja tvorjenja kloratov (V) po enačbi 3) hitro znižati na koncentracijo pod 3 g/L. Te vrste raztopin v kislem območju niso stabilne, ter jih je potrebno porabiti v nekaj urah.

Kloratne (III) raztopine za pridobivanje klorovega dioksida po peroksidisulfat-kloratnem (III) postopku naj bi imele koncentracijo pod 6 g/L, da po 100 %-tni pretvorbi klorata (III) v klorov dioksid dosežemo eksplozijsko mejo klorovega dioksida pri sobni temperaturi. Presežek natrijevega peroksidisulfata je potreben, da povečamo reakcijsko hitrost in da zagotovimo čim manjšo tvorbo kloratov (V), kot kaže enačba 22. Reakcija naj poteka v območju pH vrednosti med 5,5 in 8.

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# Izračun ogljičnega odtisa pri pretovarjanju avtomobilov v Luki Koper

## The carbon footprint calculation of cars transhipmented in Port of Koper

I. DOBNIK<sup>1\*</sup>, F. CEPAK<sup>2</sup> in B. POLJŠAK<sup>1</sup>

### POVZETEK

Povečana koncentracija toplogrednih plinov, na katere ključno vplivata prav industrija in promet, povzroča podnebne spremembe. Zato smo se v tem delu odločili preučiti obremenjenost okolja zaradi pretovarjanja vozil v avtomobilskem terminalu omenjene luke.

Namen raziskave je bil ugotoviti obremenjevanje Luke Koper oz. njene okolice z izpusti ogljikovega dioksida, ki ga emitirajo vozila pri pretovarjanju v avtomobilskem terminalu, izračunati emisijo na več različnih načinov in med seboj primerjati rezultate, ter tako dobljen segment ogljičnega odtisa primerjati s količino ogljikovega dioksida, ki ga povzročajo ostale luške aktivnosti.

Za leto 2010 smo zbrali statistične podatke o novoregistriranih vozilih v RS in podatke o pretovorjenih vozilih v Luki Koper. Pridobljene podatke o novih vozilih v Sloveniji smo preračunali na število pretovorjenih vozil v Luki Koper in izračunali, koliko ogljikovega dioksida se sprosti pri pretovarjanju vozil. V praktičnem delu smo izvedli dejanske meritve porabljenega goriva na avtomobilu. Iz izmerjene porabe goriva in emisijskih faktorjev smo izračunali emisije ogljikovega dioksida. Vse izračune smo med seboj primerjali in ocenili emisije, ki najbolj ustrezajo primeru pretovarjanja vozil v Luki Koper.

Emisije, ki smo jih izračunali na podlagi teoretičnih podatkov o emisijah in porabi goriva, znašajo 159 t/a in 160 t/a ogljikovega dioksida. Nekoliko drugačne vrednosti ogljikovega dioksida smo dobili iz izračunane porabe vozil, ki smo jih uporabili v eksperimentalnem delu naloge. Na podlagi opravljenih meritev smo izračunali, da so emisije ogljikovega dioksida kar 1.703,2 t/a, kar pomeni več kot 10-krat večje od teoretično izračunanih.

Sklepamo, da je ogljični odtis Luke Koper pri pretovarjanju vozil veliko večji, kot kažejo izračuni iz leta 2009 ali kot to lahko ocenimo na podlagi razpoložljivih podatkov.

### KLJUČNE BESEDE:

CO<sub>2</sub>, ogljični odtis, pristanišče, Luka Koper, pretovarjanje vozil, avtomobilske emisije, poraba goriva, merjenje porabe, emisijski faktor.

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## ABSTRACT

Scientists share unanimous opinion that changes are happening due to increased concentration of greenhouse effect gasses in atmosphere, mostly affected by industry and traffic. Therefore it was decided to explore effects of these two significant components on the case of the Slovenian biggest port Luka Koper. Specifically the influence of vehicles transportation in automobile terminal of Luka Koper on environment has been analyzed.

The purpose of the research was to explore what damage to environment the carbon dioxide does cause during transporting vehicles in automobile terminal. The main goal was also to calculate the emissions in several ways and afterwards compare the results of different methods. Finally the comparing of the obtained carbon footprint of transportation and the amount of carbon dioxide produced by other port's activities has been done.

The statistical data of newly licensed vehicles in the Republic of Slovenia and then the number of transported vehicles in Luka Koper in year 2010 was gained. Then the data of newly licensed vehicles were calculated in alignment with the number of transported vehicles in Luka Koper so that it was possible to calculate the amount of carbon dioxide produced by transportation of vehicles. In the empirical part of the study actually all measurement has been implemented in order to determine actual car fuel consumption and furthermore the emissions of carbon dioxide were calculated. All calculations were compared and finally the research team determined the emission amount which is closest to the case of vehicle transportation in Luka Koper.

Emission on the basis of theoretical data of emissions and actual fuel consumption is 159 t/a and 160 t/a of carbon dioxide was calculated. Results obtained by analyzing actual car fuel consumption in empirical part of the study brought us to quite different findings – the emissions of carbon dioxide found were more than ten times higher and ended up at 1.703 t/a.

It was concluded that the carbon footprint of Luka Koper's segment of vehicle transportation is much larger than the indicative calculations from year 2009 and much higher than the evaluation one could made on the basis of available data.

## KEY WORDS:

CO<sub>2</sub>, carbon footprint, port, Luka Koper, vehicle transportation, car emissions, fuel consumption, fuel consumption measuring, emission factor.



## UVOD

Skrb za okolje v družbi postaja vse bolj pereča tema mnogih razprav tako med posamezniki kot globalnimi korporacijami. Obenem se izboljšujejo razne tehnologije za zmanjševanje negativnih, nevarnih in škodljivih vplivov na okolje. Diskusijam o varovanju okolja se pridružujejo tudi različne teorije o segrevanju ozračja in povečevanju količine toplogrednih plinov, kar nas nadalje popelje na pojem t.i. ogljičnega odtisa, ki ga povzroča vsaka človeška aktivnost na planetu [1]. Ogljični odtis predstavlja določeno vrednost, ki prikazuje, koliko neka oseba, podjetje, država ali cel svet obremenjuje okolje s toplogrednimi plini [2]. Izračun svojega ogljičnega odtisa lahko danes opravi vsakdo – pa ne zgolj zase – izračuna lahko ogljični odtis za prav vsak produkt in/ali storitev. Podjetja ta pristop pogosto uporabljajo za zniževanje obratovalnih stroškov in uvajanje bolj nevtralnega delovanja v smislu okoljske ozaveščenosti. Eno izmed okoljsko zavednejših podjetij v Sloveniji je Luka Koper, ki je z namenom postati še bolj okoljsko osveščeno, v svoj dolgoročni načrt vključilo več "zelenih" projektov.

V naši raziskavi bomo izračunali le določen del ogljičnega odtisa Luke Koper, natančneje bomo proučili odtis, ki nastane pri pretovarjanju vozil v Luki Koper. Podobna študija je bila izvedena že leta 2009 (izračunan ogljični odtis za leto 2008) in sicer avtorja Uroša Luina s sodelavci in objavljena v International Journal of Sanitary Engineering Research [3]. Slednji so izračun opravili na podlagi nekaj posplošenih oziroma privzetih vhodnih podatkov, zato se bomo v nalogi lotili vprašanja, kakšen je dejanski segmentalni ogljični odtis in koliko le ta odstopa od izračuna prej omenjenega avtorja, ter kakšno je odstopanje od izračunov iz statističnih podatkov.

## METODE

Raziskava je razdeljena na dva dela. K prvemu delu smo pristopili z analizo teoretičnih podatkov, v drugem delu pa smo izvedli preizkus. Iz rezultatov obeh metod bomo ugotovili, ali nastane odstopanje med teoretičnim izračunom (iz znanih podatkov) in rezultati eksperimenta. Pri meritvah in izračunih smo upoštevali samo emisije ogljikovega dioksida, saj ima ta najpomembnejši vpliv na nastanek tople grede, tudi zaradi avtomobilskih emisij [4]. Ostale emisije kot so na primer metan in dušikovi oksidi v transportu predstavljajo le okoli 2 % emisij [5]. in so odvisne predvsem od višje delovne temperature motorja, do katerih pa pri obravnavanem primeru ne prihaja.

### **Zbiranje statističnih podatkov in teoretični pristop k izračunu emisij**

Statističnih podatkov o številu, znamki in tipu pretovorjenih vozil, ki bi nam pomagali pri natančnem izračunu emisij v Luki Koper ne vodijo, zato smo uporabili podatke o novo registriranih vozilih v Republiki Sloveniji, ki jih poseduje Ministrstvo za notranje zadeve. Iz teh podatkov smo pridobili tudi informacije o povprečni (kombinirani) porabi vozila in njihovih izpušnih ogljikovega dioksida [6].

Pri meritvah in izračunih smo upoštevali samo emisije ogljikovega dioksida, saj ima ta najpomembnejši vpliv na nastanek tople grede, tudi zaradi avtomobilskih emisij.

Podatke o številu, znamki ter modelu novo registriranih vozil v RS smo nato prenesli na primer vseh pretovorjenih vozil v Luki Koper. Evidenco o skupni količini pretovorjenih vozil smo pridobili v Luki Koper, pri čemer smo predpostavili, da je Slovenija glede nakupa novih vozil primerljiva z vsemi ostalimi evropskimi državami, za katere Luka Koper opravlja pretovarjanje vozil [7]. Torej iz tega lahko privzamemo, da je delež zastopanja določenega modela vozila približno enak po ostalih evropskih državah. Z omenjenim postopkom pridobimo podatke o tem, koliko vozil posameznega tipa je bilo pretovorjenih v Luki Koper. Iz registra podatkov Ministrstva za notranje zadeve pa pridamo še podatke o porabi goriva in emisijah ogljikovega dioksida.

Ugotoviti je potrebno še povprečno prevoženo razdaljo, ki jo vsako vozilo opravi med pretovarjanjem. Sama pot se deli na dva dela: na pot raztovarjanja (z ladje na parkirišče) in na pot prevoženo pri natovarjanju (s parkirišča na tovorno vozilo ali vlak). Pri ocenjevanju dolžine obeh poti smo se posluževali iste metodologije. S spletnim orodjem Agencije republike Slovenije za okolje smo izmerili dolžino od mesta raztovarjanja do parkirišča ter tako izračunali povprečno razdaljo, ki jo opravi vozilo pri raztovarjanju. Pri natovarjanju smo izmerili povprečno dolžino od parkirišča do najbližjega mesta natovarjanja.

Na ta način smo dobili potrebne vhodne podatke za teoretični izračun emisij ogljikovega dioksida, ki nastane pri pretovarjanju vozil (število in vrsto vozila, emisije in porabo goriva, ter prevoženo razdaljo).

S preprostimi matematičnimi enačbami smo tako izračunali emisije iz:

- količin porabljenega goriva in
- podane emisije ogljikovega dioksida iz baze podatkov.

### **Meritve porabe goriva in izračun emisij**

Dejanske meritve porabe goriva smo se lotili tako, da smo se s testnimi vozili odpeljali po vnaprej točno določeni poti in tako izmerili porabljeno gorivo. Izrednega pomena je skrbno načrtovana pot. Eksperiment smo opravili pred Zdravstveno fakulteto v Ljubljani. Pri načrtovanju poti smo upoštevali številne dejavnike, kot so: povprečna razdalja, naklon vozišča, speljevanje in ustavljanje, količina vožnje v 1., 2., 3., 4., in vzvratni prestavi, hladen vžig in vožnja s hladnim motorjem ter starost vozila. Količino porabljenega goriva smo izmerili tako, da smo rezervoar napolnili do točke, da je bila gladima goriva vidna, nivo goriva smo označili, se nato odpeljali po začrtani poti in na koncu ponovno dolili porabljeno gorivo do označenega nivoja. Količina dolitega goriva je predstavljala količino porabljenega goriva.

Izmerjeno vrednost porabljenega goriva smo primerjali s podatkom o teoretični porabi goriva, ki je podana v homologacijskem kartončku vozila in tako ugotovili odstopanje. Na podlagi dobljenih podatkov, smo izračunali dejanske količine emisij, ki nastanejo pri pretovarjanju vozil.

Vožnje smo z istimi vozili opravili večkrat in rezultati meritev porabe so med seboj primerljivi. Pri izračunu emisij iz podatkov iz eksperimental-

nega dela, smo upoštevali tudi znižanje porabe goriva zaradi višjih temperatur v poletnih mesecih.

## REZULTATI

### STATISTIČNI PODATKI

Vseh novo registriranih vozil v RS, ki ustrezajo profilu obravnavane teme v letu 2010 je bilo 60.916. V zajetih vozilih še vedno prevladuje količina vozil na bencinski pogon (63 %). V Luki Koper so v letu 2010 (leto izračuna) pretovorili kar 533.300 vozil skoraj vseh vrst avtomobilskih znamk. **Preglednica 1** prikazuje količino vozil po znamkah, ki so bila novo registrirana v RS, in kolikšen delež pretovorjenih vozil v Luki Koper v letu 2010 – glede na našo oceno – predstavljajo.

### PREVOŽENA RAZDALJA

Povprečno prevoženo razdaljo pretovorjenih vozil v Luki Koper prikazuje **preglednica 2**.

Iz izračunanih podatkov povprečne prevožene razdalje ugotovimo, da so vsa vozila v Luki Koper (za namene pretovarjanja) skupaj prevozila kar 1.102.864 km/a.

### IZRAČUNANE EMISIJE IZ PODATKOV O EMISIJI VOZILA

Iz podatka o emisiji določene znamke vozila ugotovimo, da povzroči raztovarjanje vozil v Luki Koper 121,98 t/a CO<sub>2</sub>, od tega 76,98 t/a bencinska vozila, 45,00 t/a pa dizelska. Pri natovarjanju je emisij nekoliko manj in sicer emitirajo 37,38 t/a CO<sub>2</sub>, od tega 23,59 t/a CO<sub>2</sub> bencinska in 13,79 t/a dizelska vozila.

Izračun pokaže, da vozila pri pretovarjanju obremenijo okolje za **159,36 t/a CO<sub>2</sub>**.

### IZRAČUNANE EMISIJE IZ PODATKOV O KOMBINIRANI PORABI VOZILA

Izračun na podlagi podatka o kombinirani porabi vozil pokaže podobne rezultate. Rezultati niso presenetljivi, saj so podatki o kombinirani porabi vozila prav tako teoretični iz iste baze podatkov. Je pa pokazatelj, da je bil izračun izveden brez napak.

Pri izračunu na podlagi povprečne prevožene razdalje in kombinirane porabe vozila ugotovimo, da vozila pri raztovarjanju obremenijo okolje z 122,56 t/a CO<sub>2</sub> od tega 74,83 t/a CO<sub>2</sub> bencinska in 47,74 t/a dizelska vozila. Pri procesu natovarjanja vozila skupno emitirajo 37,55 t/a CO<sub>2</sub> od tega 22,93 t/a bencinska in 14,63 t/a dizelska vozila. Tako izračunamo skupne nastale emisije, ki znašajo **160,12 t/a CO<sub>2</sub>**.

V drugem, eksperimentalnem delu, je prevožena pot z vozilom predstavljala natanko tisto pot, ki jo vozilo prevozi pri procesu raztovarjanja v Luki Koper. Po skrbno načrtovani poti smo se večkrat peljali z različnimi vozili. **Preglednica 3** prikazuje rezultate voženj s tremi različnimi vozili.

Pri procesu natovarjanja vozila skupno emitirajo 37,55 t/a CO<sub>2</sub> od tega 22,93 t/a bencinska in 14,63 t/a dizelska vozila. Tako izračunamo skupne nastale emisije, ki znašajo 160,12 t/a CO<sub>2</sub>.

**Preglednica 1:**

Pretovorjena vozila v Luki Koper.

Znamka	Števski delež		Število - Luka Koper	
	B (%)	D (%)	B	D
Alfa romeo	0,123	0,128	657	683
Audi	0,346	1,643	1.847	8.763
BMW	0,174	2,147	928	11.451
Chevrolet	2,673	0,492	14.253	2.626
Chrysler	0,149	0,007	797	35
Citroen	3,894	3,564	20.766	19.006
Dacia	0,942	0,292	5.025	1558
Daihatsu	0,003	0,000	18	0
Dodge	0,003	0,020	18	105
Fiat	4,465	0,215	23.813	1.147
Ford	4,293	1,530	22.893	8.159
Honda	0,826	0,236	4.404	1.261
Hyundai	3,492	1,313	18.621	7.004
Jaguar	0,005	0,021	26	114
Jeep	0,003	0,038	18	201
Kia	2,577	1,441	13.745	7.687
Lancia	0,044	0,016	236	88
Land rover	0,000	0,080	0	429
Lexus	0,039	0,015	210	79
Lotus	0,002	0,000	9	0
Maserati	0,005	0,000	26	0
Mazda	1,463	0,491	7.800	2.618
MB	0,363	0,878	1.935	4.684
Mini	0,207	0,003	1.103	18
Mitsubishi	0,213	0,172	1.138	919
Nissan	1,853	0,522	9.884	2.784
Opel	6,496	2,323	34.642	12.388
Peugeot	3,996	2,968	21.309	15.828
Porsche	0,033	0,026	175	140
Proton	0,005	0,000	26	0
Renault	10,830	6,085	57.755	32.454
Saab	0,013	0,008	70	44
Seat	1,763	0,639	9.403	3.406
Smart	0,018	0,007	96	35
SsangYong	0,000	0,034	0	184
Subaru	0,121	0,136	648	727
Suzuki	0,799	0,028	4.264	149
Škoda	2,531	2,090	13.500	11.145
Tata	0,025	0,007	131	35
Toyota	2,154	0,867	11.486	4.622
VW	5,687	6,561	30.326	34.992
Volvo	0,046	0,279	245	1.488
<b>SKUPAJ</b>	<b>62,675</b>	<b>37,325</b>	<b>334.245</b>	<b>199.055</b>

### Preglednica 2:

Povprečna prevožena razdalja.

Dolžina poti	Razdalja (m)
Raztovarjanje	1.583
Natovarjanje	485
Skupaj	2.068

### Preglednica 3: Rezultati praktičnih presizkusov porabe goriva.

Gorivo	Vozilo	Porabljeno gorivo (mL)	Spec.poraba (L/100 km)	Predvodena poraba (L)	Faktor odstopanja
Dizel	Nissan Qashqai	1.170	5,2	0,091	12,857
	Seat Leon	660	4,8	0,076	8,684
Bencin	Toyota Yaris	940	5,1	0,081	11,605

Ugotovili smo tudi, da se je poraba vozila (na naši relaciji), ko je bilo slednje ogreto na svojo delovno temperaturo, znižala kar za polovico.

Iz eksperimentalnega dela ugotavljamo, da je dejanska poraba dizelskega goriva za 10,5 krat, bencinskega pa kar za 11,5 krat večja od teoretično izračunane. Iz česar sledi, da je dejanska obremenitev okolja zaradi pretovarjanja vozil veliko večja, kot smo predvidevali (iz teoretičnega izračuna ter rezultatov raziskave iz leta 2009). Iz eksperimentalnega dela izračunane emisije znašajo kar dobrih **1.700 t/a CO<sub>2</sub>**. Pri izračunu smo tudi upoštevali korekcijske faktorje za toplejše mesece v letu, saj je poraba goriva odvisna tudi od temperature okolice.

## DISKUSIJA

Pri obdelavi statističnih podatkov je njihova kakovost ključnega pomena. Model je vedno le približek realnega stanja. Najbolje bi bilo, če bi podatke vodili v sami Luki. Le ti bi bili izjemno točni in veliko lažje bi jih bilo obdelati. Ker takšnih podatkov ni, so bili v izračun zajeti podatki Ministrstva za notranje zadeve RS. Podatki so verodostojni in jih lahko prenesemo na primer izračuna pretovora v Luki Koper, saj je indeks novo registriranih vozil za Slovenijo, ki ga tudi za vsako drugo državo članico EU vodi Eurostat, primerljiv z ostalimi Evropskimi državami [7].

Zaradi podatkov o emisijah in podatkov o povprečni porabi lahko teoretični izračun z nekaj enačbami natančno izvedemo. Toda kako realen je takšen izračun glede na dejansko stanje? Kot vemo je pri porabi goriva, odstopanje od primera do primera lahko znatno. Obenem je visoko tudi število dejavnikov, ki vplivajo na porabo goriva. Pri pretovarjanju vozil v Luki gre za izjemno sofisticiran primer, zato je še toliko bolj pomembno, da se ocena ogljičnega odtisa za ta segment podkrepiti s konkretnimi eksperimentalnimi meritvami.

Osnovna vhodna spremenljivka za izračun emisij je tudi prevožena razdalja. Le to je težko določiti za vsako od več sto tisoč vozil. Še posebej, ker gre v Luki za zelo obsežno dejavnost, ki se razprostira na veliki površini. Pri prevozu vozil po Luki je mogoče obrati več poti, zato je up-

Pri izračunu smo tudi upoštevali korekcijske faktorje za toplejše mesece v letu, saj je poraba goriva odvisna tudi od temperature okolice.

Tako so rezultati pokazali, da je segmentalni ogljični odtis zaradi pretovarjanja vozil v Luki Koper kar 1.700 t/a ogljikovega dioksida.

orabljen pristop izračuna in določitve povprečne razdalje za vsa vozila najbolj primeren. Napaka, ki pri tem nastane, je zanemarljiva.

V izračunu emisij v prvem delu sta uporabljena vhodna podatka emisija ogljikovega dioksida in kombinirana poraba. Oba podatka izvirata iz statističnih podatkov in sta izmerjena oziroma določena skorajda v idealnih pogojih. Problem nastane, ker je primer v Luki Koper vse drugo kot pa idealna prevožena pot. Tukaj imamo v mislih predvsem vožnjo vozil na kratke razdalje, vožnjo s hladnimi motorji ter predvsem veliko ustavljanja in speljevanja. Zaradi takšnih pogojev nam vpogled v dejansko stanje izostri prav eksperimentalni del, ki pokaže, da so dejanske emisije veliko večje kot bi sklepali iz teoretičnega izračuna.

Tako so rezultati pokazali, da je segmentalni ogljični odtis zaradi pretovarjanja vozil v Luki Koper kar 1.700 t/a ogljikovega dioksida. Pri tem pa niso bili upoštevani še ostali toplogredni plini iz transporta, čeprav je teh manj oz. so nižje. Če bi v študiji zajeli še te, bi bila končna vrednost emisij še nekoliko višja.

Za še natančnejši izračun bi bilo potrebno opraviti eksperimentalni del na konkretnih vozilih, ki se jih pretovarja v Luki Koper. Eksperiment bi bilo potrebno ponoviti v različnih letnih časih z istimi tipi vozil in nato med seboj primerjati rezultate. Izračun bi bil še nekoliko bolj natančen, verjetno pa odstopanje ne bi bilo veliko.

Vrednost ogljičnega odtisa (za pretovarjanje vozil) izračunanega na podlagi pridobljenih statističnih podatkov znaša 160 t/a CO<sub>2</sub>. Po izračunu za leto 2008 [3] je bil ogljični odtis 480 t/a CO<sub>2</sub>. Pretovor vozil v letu 2008 je primerljiv s količino pretovorjenih vozil v naši raziskavi. Iz eksperimentalnega dela izračunana vrednost ogljičnega odtisa pa znaša kar 1.700 t/a.

Zakaj nastane takšna razlika?

V prvem delu, t.j. 160 t/a ogljikovega dioksida, je to vrednost, ki temelji zgolj na statističnih podatkih. Le ti so večinoma pridobljeni od proizvajalcev vozil, ki pa si prizadevajo, da bile te vrednosti čim nižje in jih ponavadi podajajo na podlagi meritev v idealnih pogojih. Pri pretovarjanju vozil pa gre za poseben primer, v katerem se od idealnih pogojev za vožnjo kar precej oddaljujemo. Izračunana vrednost je tako nizka zaradi neupoštevanja dejavnikov, ki pomembno vplivajo na porabo goriva in avtomobilske izpuste. Druga vrednost, ki je razvidna iz študije Luin in sodelavcev [3], temelji na nekaterih privzetih vrednostih, kot sta na primer kombinirana poraba in povprečna prevožena razdalja. Ti podatki niso natančni in ne morejo zagotoviti točnega izračuna. Tretja izračunana vrednost iz eksperimentalnega dela, pa predstavlja realno stanje v pristanišču. Vozila, ki jih vozijo po parkiriščih, se vozijo na kratkih razdaljah, z veliko zaviranjem in speljevanjem, ter morda najpomembnejše, s hladnimi motorji. To so trije poglobitni razlogi, zaradi katerih se izračunane vrednosti tako razlikujejo. Dejstvo pa je, da je emisij veliko več, kot smo pričakovali. Eksperimentalni del bolje odraža dejansko stanje in poda realno oceno ogljičnega odtisa.

Hkrati se je potrebno zavedati, da izračunani segmentalni ogljični odtis 1.700 t/a ogljikovega dioksida predstavlja le okoli 3 % celotnega odtisa Luke, kar nakazuje, za kako veliko dejavnost dejansko gre. Zanimiv podatek je tudi ta, da so vozila v letu 2010 kot posledica pretovarjanja naredila toliko kilometrov, kot če bi 27-krat obkrožili naš planet po ekvatorju. Če bi Luka Koper želela nevtralizirati segmentalni ogljični odtis, nastal zaradi pretovarjanja vozil v Luki Koper, bi morala posaditi 1.700 dreves.

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Če bi Luka Koper želela nevtralizirati segmentalni ogljični odtis, nastal zaradi pretovarjanja vozil v Luki Koper, bi morala posaditi 1.700 dreves.

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