ZESZYTY NAUKOWE AKADEMII MARYNARKI WOJENNEJ
SCIENTIFIC JOURNAL OF POLISH NAVAL ACADEMY

2017 (LVIII) 1 (208)

DOI: 10.5604/0860889X.1237621

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POLLUTIONS OF THE HYPERBARIC BREATHING ATMOSPHERE

ABSTRACT

The Sweedish project codenamed DykSMART was carried out in 2013–2015. The results of this project created the base for for international project #R024 *Diving with State Maritime Resources in the Baltic DiveSMART-Baltic of Interreg Baltic Sea Region* launched in 2016. The Interreg Baltic Sea Region Programme 2014–2020 supports the integrated territorial development and cooperation for a more innovative, better accessible and sustainable Baltic Sea region. Partners from the countries around the Baltic Sea work together in transnational projects on common key challenges and opportunities.

DiveSMART project is dedicated to improved coordination concerning the organizations with emergency divers, in order to be able to handle an international emergency situation:
- to be aware of which diving competences are available, and also relevant diving equipment;
- common international exercises;
- knowledge of education and definitions of various levels of competence;
- research & development.

The project DiveSMART Baltic has received Flagship status. The article is the first in the planned cycle of articles referring to the tasks realised in the Naval Academy within the framework of DiveSMART project. This article presents a review of pollutants of the hyperbaric breathing agent in connection with their toxic action. This subject is linked to the work package four of the DiveSMART project *Risk reduction — develop and enhance methods for life support systems of distressed persons in both physical and psychological areas*.

Key words:
hyperbaric atmosphere, underwater hyperbaric survival, breathing air pollutants.

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INTRODUCTION

An unexpected air hyperbaric exposition can occur as a result of submarine damage or survival of people in air traps following sinking of a surface vessel.

In the case of a submarine the crew is trained in damage control (survival) procedures, has access to rescue equipment and the submarine has resources designed to cope with some damage scenarios. An increase in pressure in one of the compartments may not affect the whole vessel. The vessel can retain some energy supplies and the crew can seal the vessel, and using compressors can put decompression under control. When the damage is extensive the crew has equipment which can be used to escape to the surface, preventing, in this way, their organisms from becoming saturated.

There do not exist any dedicated elements of the rescue system which people who have got stuck together with the sunken surface vessel could use to counter the effects of air saturation hampering the rescue operation. So far chances for survival of victims under such conditions have been viewed with skepticism. However the case of 'Harrison Okene' who survived for more than 62 hrs in a sunken tugboat 'Jascon-4', which had sunk in the Atlantic on 26 May, 2013 at the depth of 30 mH_2O about 30 km off the Nigerian coast requires a change in approach to this issue.

JUSTIFICATION

The Baltic Sea is a crowded area. European economies use this region for transporting goods and people. Both communication lanes, to a large extent, crisscross. Goods are carried in the direction of East-West whereas transport of people in the direction of North-South — figure 1. Hence there exist a substantial risk of collision in which a lot of people will die, including those caught in air traps in a wreck.

Looking at an example of daily vessel traffic in the Baltic Sea shown in figure 2 a conclusion can be drawn that this area is, to a large extent, empty enough to not cause a risk of collision. However, taking into account the accident which happened 3 Nm off the North-West coast of Bornholm at 12:08 on 31th May, 2003, where two vessels collided: 225 m long Panama type 'ms Fu Shan Hai' and container vessel 'ms Gdynia', under perfect visibility conditions, we should be aware that such collisions may occur in future.

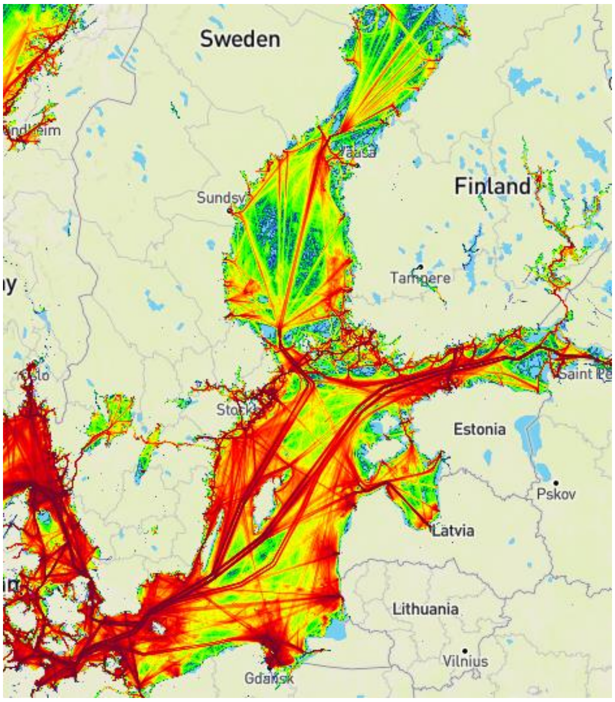

Fig. 1. Vessel traffic density in the Baltic in 2015
[http://www.marinetraffic.com/pl/ais/home/centerx:18/centery:58/zoom:5 (access 06.12.2016)]

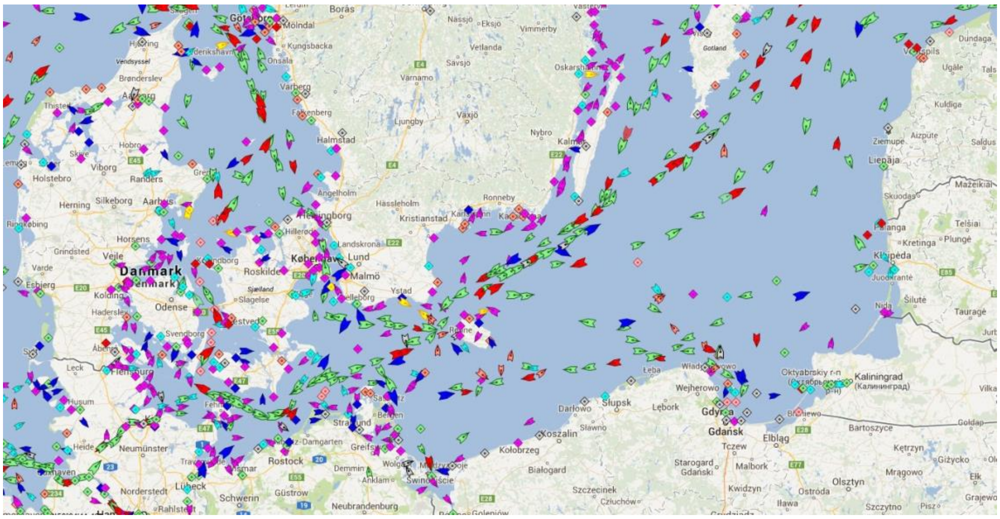

Fig. 2. Example of daily vessel traffic in the Baltic
[http://www.marinetraffic.com/pl/ais/home/centerx:15/centery:55/zoom:8 (access 06.12.2016]

As the case of 'Harrison Okene' shows there exists a possibility for people to survive in air traps in a sunken vessel. The situation of the survivors would be unenviable. Without developing underwater rescue capabilities effective help to such survivors is rather doubtful.

Part of knowledge and technical infrastructure has been developed by navies for rescuing submarine crews. However, the scenario of a rescue operation after the pressure in a submarine has risen and the crew have been saturated remains unsolved because the absence of capabilities to transport them.

Therefore, a solution to the problem of survivors trapped in air bubbles inside a sunken vessel, and exposed to saturation, will be a double-purpose technology, used to rescue both crews from submarines as well as survivors from both civilian and naval surface vessels.

Solution to this problem situation will have to be based on military projects in case of failure to carry out this project.

Until not a long time ago Europe enjoyed the period of détente between the superpowers. This resulted in reducing defense spending. First, reductions affected those activities which caused lowest dissatisfaction on the part of military personnel i.e. those which did not directly lead to reduction in military personnel. These policies resulted in limiting areas of R&D activities. Some countries, like Great Britain, privatized the whole fields of R&D activities in the armed forces. For example, 'QinetiQ' was privatized. Also, defense-industry partnerships started to be established. For example, after the US stopped providing support for the world rescue system with deep submergence rescue vehicles 'DSRV[1] Mystic' and 'DSRV Avalon' (fig. 3) and after 'ASRV[2] Remora' (fig. 4) systems was scrapped, following an accident a partnership focused on developing submarine rescue systems 'NSRS'[3] (fig. 5) was established. However, most hyperbaric R&D establishments have lost their donations and stopped carrying out their tasks connected with underwater rescue. It is hard to say if the research will be resumed at present.

At the moment research is being carried out on submarine crew rescue using 'NSRS' by a British-French-Norwegian consortium. The problems investigated are related, however, to rescuing submarine crews when it is possible to secure the submarine to the rescue vessel. In such a situation scenarios of decompression acceleration or other forms of optimizing a rescue operation can be worked out.

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[1] Deep Submergence Rescue Vehicle.

[2] **A**ustralian **DSRV**.

[3] **N**ATO **S**ubmarine **R**escue **S**ystem.

Fig. 3. 'DSRV Mystic' on board the submarine used the base for its operations [https://en.wikipedia.org/wiki/DSRV-1_Mystic#/media/File:DSRV-Mystic.jpg (access 06.12.2016)]

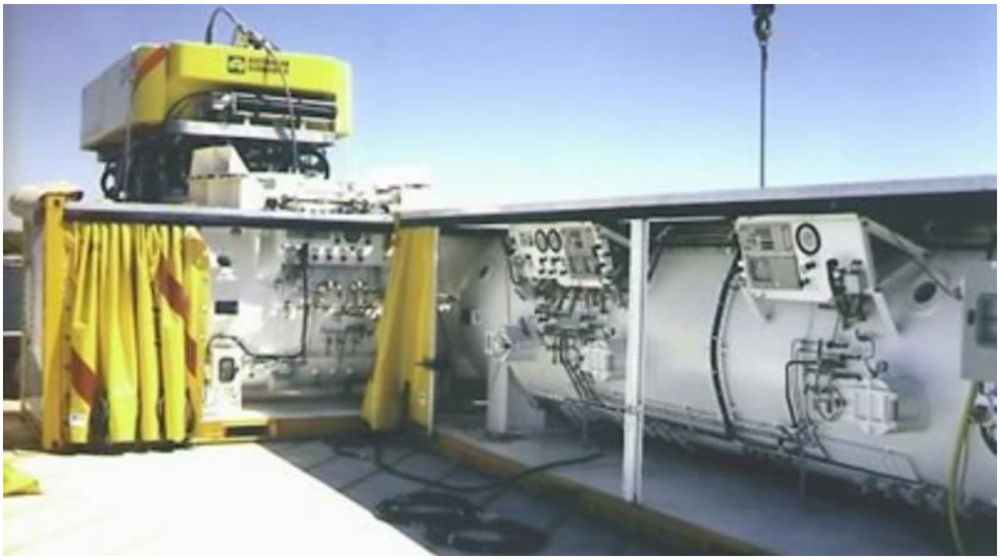

Fig. 4. 'ASRV Remora' together with hyperbaric chambers [http://www.idpm.biz/windows/image9.htm (access 06.12.2016)]

Fig. 5. NSRS rescue vehicle [https://en.wikipedia.org/wiki/File:NATO_Submarine_Rescue_System_(NSRS)_MOD_45152366.jpg (access 06.12.2016)]

The scenario of increasing pressure in a sunken submarine when the docking area for a submersible vehicle is damaged and the possibility of using the procedure for free surfacing is absent is the same as for the survivors trapped in an air trap inside a sunken vehicle. Such scenario of an underwater rescue operation is at present being investigated under the DiveSMART-Baltic within the framework of Interreg-Baltic program.

At present transfer of the so called dual purpose technologies from the armed forces to civilian environment has become significant, following the idea that armed forces are used not only for defense purposes but also serve the homeland and nation during peacetime.

Economic growth in many countries has often been successfully stimulated through government defense orders and defense focused R&D programs. Tax payers' money is used to finance streams of goods produced, as an added value, through carrying out defense related projects. It has been noticed that these goods can serve not only defense purposes generating return on the investments made. Rescue undoubtedly belongs to such fields of activity. Therefore, transfer of the results obtained under rescue projects is not only morally and economically justified but it is simply necessary.

In recent years Poland has consistently maintained its defense budget at a relatively high level and Sweden has recently doubled its own. This generates a good situation for defense focused projects, which should be taken into consideration when carrying out this project and other related projects.

A review of pollutants of the breathing agent has been made with regard to their toxic action has been presented in the article. This subject is connected to the work package four ‘Risk reduction’ of the ‘DiveSMART’ project: Develop and enhance methods for life support of distressed persons in both physical and psychological areas.

BREATHING AGENT POLLUTANTION

Pollution of a breathing agent by components causing toxic action on human organism is always undesirable. Generally, it can be assumed that the response of an organism to a toxic component in the form of vapor or gas is dependent on its partial pressure: $p_i \equiv p \cdot x_i$, where: p_i — partial pressure of the *i*th component $[Pa]$, p — total pressure of gas mixture $[Pa]$, x_i — mole fraction of the *i*th component $[mol \cdot mol^{-1}]$. If for the atmospheric pressure p_0 the acceptable content of a component is equal to $x_i^{max} = x_i$, for the pressure equivalent to the depth of $10\ mH_2O$ the acceptable content of this component is half lower: $x_i^{max} = 0{,}5 \cdot x_i$. If in the breathing agent there occur more than type of pollutants, the law of cumulative pollution action is applied [1]: $\sum_i \frac{x_i}{x_i^{max}} \leq 1{,}3$. Some authors recommend adopting magnitude 1,0 instead of 1,5. The maximum acceptable concentration C_i^{max} of the toxic substances is usually calculated in relation to the atmospheric pressure p_0. Using the definition of partial pressure it is possible to calculate the maximum pressure p_i^{max} for toxic substances: $p_i^{max} = p_0 \cdot \frac{C_i^{max}}{100\%}$. Using the definition of percentage concentration $C_i \stackrel{\text{def}}{=} x_i \cdot 100\%$, the following can be written:

$$\sum_i \frac{C_i}{C_i^{max}} = \sum_i \frac{x_i}{x_i^{max}} = \sum_i \frac{p_i}{p_i^{max}} \leq 1{,}5, \tag{1}$$

where:

C_i — concentration of the *i*th polluting component $[\%_{obj.}]$;
C_i^{max} — maximum acceptable concentration of the *i*th polluting component $[\%_{obj.}]$;
x_i — mole fraction of the *i*th polluting component $[mol \cdot mol^{-1}]$;
x_i^{max} — maximum acceptable mole fraction the *i*th polluting component $[mol \cdot mol^{-1}]$;
p_i — partial pressure of the *i*th polluting component $[Pa]$;
p_i^{max} — maximum acceptable partial pressure of the *i*th polluting component $[Pa]$.

As the partial pressure of the toxic substance i is $p_i = p_0 \cdot \frac{c_i}{100\%}$, the dependence (1) can be written for hyperbaric conditions:

$$\frac{p}{p_0} \sum_i \frac{c_i}{c_i^{max}} \leq 1{,}5, \tag{2}$$

where:
p — total pressure at the depth of diving [Pa].

Air pollution in an ecologically closed atmosphere can be divided into three groups:
- pollutants caused by air;
- pollutants caused by technical elements being in contact with a breathing agent[4];
- pollutants caused by human organism.

Pollutants caused by breathing air

Typical pollutants caused by breathing air are: carbon dioxide $< 0{,}05\%_{obj.}$, nitrogen oxides $< 0{,}7\, mg \cdot m^{-3}$, hydrocarbons $< 5{,}0\, mg \cdot m^{-3}$, carbon oxide $< 3{,}0\, mg \cdot m^{-3}$,water vapor $[0{,}01 - 0{,}1]\, g \cdot m^{-3}$ etc. The composition of dry air is shown in table 1.

Tab. 1. Composition of dry air in volume and mass percentage [own work]

Gas	N_2	O_2	Ar	CO_2	H_2	Ne	He	Kr	Xe
$C\ [\%_v]$	78.03	20.99	0.93	0.030	0.01	0.018	0.0005	0.001	0.00001
$C\ [\%_v]$	75.47	23.20	28	0.046	0.001	0.0012	0.0001	0.0003	0.0004

Pollutants caused by technical equipment

Classification societies provide typical types of pollutants caused by technical equipment and their maximum acceptable concentration magnitudes. The review of the selected pollutants coming from technical equipment is illustrated in table 2 [2]. Data on safe concentration of pollutants can be found in some instruction manuals dealing with the issue of survival in special conditions, e.g. (Военное Издательство 1983 [RBŽ-PL-82 1983]).

[4] E.g. volatile components of paints, volatile components of thermal insulation, maintenance preparations, etc.

Tab. 2. Maximum acceptable concentration of some toxic substances in submersible objects[5] [2]

Chemical compound		Source of pollution	Maximum acceptable concentration for the moment of exposition		
			1 hrs	24 hrs	90 $days$
acetylene	C_2H_2	fried dishes	6000 ppm	6000 ppm	6000 ppm
acrolein	CH_2CHCHO	fried dishes	—	0.1 ppm	—
isopryl alcohol	C_3H_7OH	paint diluent	—	—	1 ppm
ammoniac	NH_3	metabolism	400 ppm	50 ppm	25 ppm
stibine	SbH_3	battery gassing	—	0.05 ppm	0.01 ppm
arsine	AsH_3	battery gassing	—	0.1 ppm	0.1 ppm
benzene	C_6H_6	diluent	—	100 ppm	0 ppm
methyl chloride	CH_3Cl	diluent	—	—	25 ppm
chloroform	$CHCl_3$	diluent	—	—	1 ppm
hydrogen chloride	HCl	freon decomposition	10 ppm	4.0 ppm	0 ppm
nitrogen dioxide	NO_2	genreators	10 ppm	0 ppm	0.5 ppm
sulphur dioxide	SO_2	sanitation	10 ppm	5.0 ppm	0 ppm
carbon dioxide	CO_2	metabolism	2.5%	0%	0.5%
ethanol	C_2H_5OH	diluent	—	—	100 ppm
hydrogen fluoride	HF	freon decomposition	8 ppm	1,0 ppm	0,1 ppm
formaldehyde	$HCHO$	ready-made dishes	5 ppm	5 ppm	5 ppm
phosgene	$COCl_2$	freon decomposition	0 ppm	0.1 ppm	0.05 ppm
freon 113	$CClF_2CCl_2F$	coolingh installations	—	—	100 ppm
freon 11	CCl_3F	colling installations	—	—	100 ppm
freon 12	CCl_2F_2	coolling installations	—	—	100 ppm
freon 114	$CClF_2CClF_2$	colling installations	—	—	100 ppm
methyl-ethyl ketone	$CH_3COC_2H_5$	diluent	—	—	20 ppm
methyl-isobutyl ketone	$CH_3COC_3H_7$	diluent	—	—	20 ppm
xylene	$C_6H_4(CH_3)_2$	paint diluents	—	—	50 ppm
methane	CH_4	sanitation	3%	3%	3%
methanol	CH_3OH	diluent	-	-	10 ppm
ozone	O_3	commutated motors	0 ppm	0.1 ppm	0.02 ppm
nitrogen oxide	NO	generators	10 ppm	0 ppm	0.5 ppm
toluene	$C_6H_5CH_3$	diluents	—	—	20 ppm
trimethylobenzenes	$C_6H_3\ (CH_3)_3$	diluents	—	—	3 ppm
aromatic hydrocarbons except benzene		paint diluents	—	—	10 $mg \cdot m^{-3}$
aliphatic hydrocarbons except methane		paint diluents	—	—	10 $mg \cdot m^{-3}$
hydrogen	H_2	battery gassing	1000 ppm	1000 ppm	1000 ppm

Table 3 contains the maximum acceptable concentration of some toxic vapors and gases used in struggle for survival. These magnitudes are used in the formula for cumulative action of pollutants (1)—(2). Table 4 contains the maximum acceptable concentration confirmed with modern research methods and legally approved limits for concentration of selected toxic compounds in the environment, which in everyday time-limited exposition do not cause, in a longer period, pathological changes or diseases in present and future generations.

[5] Normal conditions.

Tab. 3. Maximum acceptable concentration of some toxic vapors and gases used in struggle for survival [3]

Time	Carbon oxide	Nitrogen oxides	Benzene	Toluene	Xylene	Formaldehyde	Acetaldehyde
$[min]$	$[mg{\cdot}m^{-3}]$						
5	700	60	—	—	—	—	—
10	600	45	90	—	—	—	—
15	400	35	70	270	—	—	—
20	360	30	60	—	—	—	—
30	300	25	50	170	130	8	100
40	240	20	45	—	—	—	—
60	200	15	37	165	123	—	—
120	150	—	25	115	110	—	—
240	100	—	15	80	90	—	—
480	60	10	—	—	79	—	—
1440	40	—	—	—	60	—	—

Tab. 4. Maximum acceptable concentration of selected toxic compounds for work environment [3]

Chemical compound		Maximum acceptable concentration for the time of exposition $[mg{\cdot}m^{-3}]$			
		$4\ hrs$	$8\ hrs$	$24\ hrs$	$[2000; 3000]hrs$
stibine	SbH_3	0.5	0.3	0.15	—
arsine	AsH_3	—	0.1	—	0.003
benzene	C_6H_6	—	5	—	2
phosgene	$COCl_2$	—	0.5	—	—
freon 12	CCl_2F_2	6000	3000	—	150
freon 114	$CClF_2CClF_2$	—	1000	—	100
xylene	$C_6H_4(CH_3)_2$	—	50	—	12
mercury	Hg	—	0.01	—	0.003
nitrogen oxide	NO	5	5	—	0.5
carbon oxide	CO	30	20	18	5
toluene	$C_6H_5CH_3$	—	50	—	8
hydrocarbons	C_xH_y	—	300	—	35

Tables 2 and 3 present examples of acceptable equivalent content magnitudes x_{SEV} for selected pollutants for various exposition periods. The measurement results of concentration of polluting substances x can be applied to calculate the maximum safe depth for using a breathing agent p_H with regard to equivalent content SEV [6] of toxic substance x_{SEV}:

$$p_H = \frac{x_{SEV}}{x} \cdot p_0, \tag{3}$$

[6] Surface Equivalent Value.

where:

x_{SEV} — equivalent content of pollutant [ppm_v^{SEV}];
x — content of pollutant in sample [ppm];
p_H — total hyperbaric pressure [Pa];
p_0 — normal pressure [Pa].

Pollutants whose source is human organism

In order to analyze the survival a model was developed of pollution emitted by a 'standard human being', engaged only to very light work, is presented in table 5 [1].

Use of oxygen and emission of carbon dioxide can be substantially reduced by being in the totally non-active state (tab. 6). The investigations show that in the condition of non-activity use of oxygen can be at the level of 18,7 $dm^3 \cdot hour^{-1} \cdot person^{-1} STP$ [7], and carbon dioxide emission at the level of 17,0 $dm^3 \cdot hour^{-1} \cdot person^{-1} STP$ [5]. There can occur higher magnitudes of oxygen use at the level of 30,0 $dm^3 \cdot hour^{-1} \cdot person^{-1} STP$ and carbon dioxide emission at the level of 25,0 $dm^3 \cdot hour^{-1} \cdot person^{-1} STP$. Survival is possible as long as partial pressure of oxide can be maintained above $p_{O_2} \gtrsim 16\ kPa$, and partial pressure of carbon dioxide up to the level of $p_{CO_2} < 2{,}5\ kPa$.

Short-term conditions under which survival is possible are regarded those where partial pressure of oxygen is at the level of $p_{O_2} \geq 14\ kPa$, and of carbon dioxide has not exceeded $p_{CO_2} \leq 5\ kPa$. At present it is claimed that action of small concentration of volatile hydrocarbon pollutants of a breathing agent on a human organism usually have a narcotic character[8]. It is high concentration magnitudes that act toxically [6].

Tab. 5. Pollutants emitted by a 'standard human being' under the condition of little effort [1]

Pollutant		Emission of pollutant over 24 hrs period
carbon dioxide	CO_2	550 dm^3
methane	H_4	3 dm^3
carbon oxide	CO	0.7 dm^3
aceton	$(CH_3)_2CO$	0.0005 dm^3
water vapor		2000 dm^3
Heat emission: - latent heat - the other heat		 5600 kJ 6300 kJ

[7] Standard Temperature and Pressure — STP.
[8] Anaesthetic.

Tab. 6. Streams of used oxygen and lung ventilation depending on physical effort [4]

Physical effort		Stream of used oxygen	Number of breathes per minute	Lung ventillation	Border stream of used oxygen
Intensity	Example	$[dm^3 \cdot min^{-1}]$	$[min^{-1}]$	$[dm^3 \cdot min^{-1}]$	$[dm^3 \cdot min^{-1}]$
very light	lying on bed	0.25	do 20	8–10	do 0.5
	sitting stil	0.30			
	standing still	0.40			
light	walk 3,5 $km \cdot h^{-1}$	0.7	20–25	10–20	0.5–0
moderate	march 6,5 $km \cdot h^{-1}$	2	25–30	20–30	0–5
hard	swimming at speed of 3,0 $km \cdot h^{-1}$	8	30–35	30–50	5–2.0
very hard	running at speed of 13 $km \cdot h^{-1}$	2.0	35–40	50–65	2.0–2.5
extremally hard	running uphill	4.0	>40	>65	>2.5

CONCLUSIONS

Possibilities for survival in an air trap in a sunken vessel generate a multi-threaded problem situation. Most of hazards to health and life concerned with survival affect survivors through appropriate agents acting on them. Of them the most important are: pressure, composition of breathing atmosphere, and cooling. Although maintaining mental balance in survivors and rescuers is not directly connected with the physical action, it is a very important issue. All these aspects should be taken into account in conducting an underwater rescue mission.

One of the issues discussed briefly in this article is assessment of hazard of toxic pollutants that can occur in a breathing agent. It discusses the initial analysis of breathing agent pollutants which can possibly occur and their action on a human body. Many of them are dependent on time and they are connected with each other in an interactive manner. These issues are not dealt with in here as they will be the subject of further analyses concerned with toxicity of the main components of the breathing agent, i.e. oxygen and nitrogen.

This article is an introduction to the cycle synthetically describing the results of the tasks carried out at the Naval Academy within the framework of DiveSMART project. As the first article of the planned cycle it also contains a short introduction to the project as a whole. Other issues, such as e.g. risk analysis in the project, will be interwoven when other detailed tasks are described carried out under the project.

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ZANIECZYSZCZENIA HIPERBARYCZNEJ ATMOSFERY ODDECHOWEJ

STRESZCZENIE

W latach 2013–2015 w Szwecji prowadzony był krajowy projekt pod akronimem DykSMART. Rezultaty tego projektu tworzą bazę pod międzynarodowy projekt #R024 *Nurkowanie z wykorzystaniem służb państwowych rejonu Bałtyku DiveSMART-Baltic programu Interreg Baltic Sea Region* uruchomionego w 2016 roku. Program Interreg Baltic Sea Region w perspektywie 2014–2020 wspiera zintegrowany rozwój terytorialny i współpracę na rzecz bardziej innowacyjnego, lepiej dostępnego i trwałego rozwoju regionu Morza Bałtyckiego. Partnerzy z krajów nadbałtyckich współpracują w międzynarodowych projektach dotyczących wspólnych kluczowych wyzwań i możliwości regionu.

Projekt DiveSMART służy polepszeniu koordynacji w sytuacji kryzysowej podczas międzynarodowej organizacji akcji z wykorzystaniem nurków służb państwowych poprzez:
– określenie dostępnych kompetencji i wyposażenia nurkowego;
– organizację ćwiczeń międzynarodowych;
– określenie systemów szkoleń narodowych prowadzących do różnych poziomów umiejętności nurkowych;
– badania naukowe i rozwój.

Projekt DiveSMART uzyskał status projektu flagowego. Artykuł jest pierwszym z cyklu referujących jego postępy w ramach zadań zlecanych Akademii Marynarki Wojennej. W artykule zaprezentowano

przegląd zanieczyszczeń hiperbarycznej atmosfery oddechowej z uwzględnieniem ich toksycznych właściwości. Zadanie to dotyczy czwartego pakietu roboczego projektu DiveSMART *Zmniejszenie ryzyka — opracowywanie i ulepszanie systemów zachowania życia osób narażonych na niekorzystne oddziaływania fizyczne i psychologiczne*.

Słowa kluczowe:

atmosfera hiperbaryczna, przetrwanie w podwodnych warunkach hiperbarycznych, zanieczyszczenia powietrza oddechowego.