Assessment of Work Environment Hazards during Shale Fuel Oil Handling

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Abstract. **Oil shale is the main natural commodity of Estonia. In the present paper the chemical hazards in the air of the work environment during handling of shale fuel oil are investigated.**

Research focus: the implementation of the flexible risk assessment model worked out in Tallinn University of Technology for assessment of toxic chemicals, the matrix on the basis of the five-step risk assessment model is presented, where the relationship between the exposure concentration and potential health impairment is given.

Research methods and materials: 1) the five-step flexible risk assessment model is used; 2) the measurement methods used in the study comprise: a) the gas chromatography-mass spectrometry (GC-MS) to separate the shale fuel oil; b) Dräger tubes for determination the content of chemicals in the air of the work environment.

Results: the relationship between the exposure concentration and potential health impairment is given. The occupational illness stages are developed using statistical data of diagnoses of occupational diseases.

Conclusion: according to the proposed model, the exposure to toluene and xylene poses justified risk (risk level II), benzene and phenol unjustified risk (risk level III).

Recommendations: without any additional control measures applied, the risk for occupational diseases caused by these chemicals is significant; the personal protective equipment should be provided to the workers.

Keywords**: shale fuel oil, workplace air, toxicity of chemicals, influence on health.**

I. Introduction

Estonian oil shale is the main national commodity in the country. Oil shale has been extracted for centuries. It was discovered in the North of Estonia more than 200 years ago. At the present time the Estonian government invests to the use of oil shale in the form of oil. It is used as fuel in industrial furnaces, possible for the use as cars' fuel in the future. In comparison to similar petroleum-based fuels, it is characterised by its low viscosity and low sulphur content [1], [2]. The shale fuel oil contaminates the environment less than the solid oil shale.

The current paper describes the investigations carried out in Tallinn University of Technology for determination of the content of gaseous phase formatting during handling of shale fuel oil.

Based on the WEC 2007 report, Estonia was the world's largest producer of shale fuel oil, producing 345,000 ton of shale fuel oil per year. Approximately 8000 ton of shale fuel oil was utilized for domestic electricity generation, 98,000 ton of oil for heat generation and the remaining 222,000 were exported [3].

The aim of the study was to determine the toxicity and concentration of hazardous gaseous components in the work area during handling of shale fuel oil and work out the matrix for connections between the toxic components' concentrations and possible health damages.

II. Health Hazards of the Chemicals

The chemicals with the major concern in the study are toluene, xylene, benzene and phenols. Next, a short review is presented of these 4 chemicals and their toxic effects as well as concentrations in order to be able to integrate their hazards to a workplace risk assessment model [4], [5].

The relative humidity may influence the worker's health and comfort as too dry air can cause local irritation of mucosa, eyes and skin. The overall symptoms are dizziness and headache. In the case of too humid air, the sensitiveness to the odours (gases, vapours) from the finishing materials will increase [6].

2.1. Health hazards of benzene

The short-term breathing of high levels of benzene can result in death; low levels can cause drowsiness, dizziness, rapid heart rate, headaches, tremors, confusion, and unconsciousness. Eating or drinking foods containing high levels of benzene can cause vomiting, irritation of the stomach, dizziness, sleepiness, convulsions, and death [7]. The major effects of benzene are manifested via chronic (long-term) exposure through the blood. Benzene damages the bone marrow and can cause a decrease in red blood cells, leading to anaemia. It can also cause excessive bleeding and depress the immune system, increasing the possibility for infection. Benzene causes leukaemia and is associated with other blood cancers and pre-cancers of the blood [8]. Human exposure to benzene is a global health problem. Benzene targets liver, kidney, lung, heart and the brain and can cause DNA strand breaks, chromosomal damage, etc. Benzene causes cancer in both animals and humans. Benzene has been shown to cause cancer in both sexes of multiple species of laboratory animals exposed via various routes. Benzene exposure has been linked directly to the neural birth defects. Men exposed to high levels of benzene are more likely to have an abnormal amount of chromosomes in their sperm, which impacts fertility and fetal development. Animal studies have shown low birth weights, delayed bone formation, and bone marrow damage when pregnant animals breathed benzene. Benzene has been connected to a rare form of kidney cancer in two separate studies, one involving tank truck drivers, and the other involving seamen on tanker vessels, both carrying benzene-laden chemicals [8].

2.2. Health hazards of toluene

Inhalation of toluene vapour can affect the central nervous system [9]. No toxicity was observed in human beings repeatedly exposed to toluene levels of less than 188 mg/m^3 (50 ppm) for short periods of time or exposed once to a level of 375 mg/m^3 for a few hours [10]. At approximately 188 mg/m^3, subjective complaints such as slight drowsiness and very mild headache have been reported. Mild irritation of the nose, throat, eye and respiratory tract has occurred between 375 to 750 mg/m^3. Concentrations of about 375 mg/m^3 have caused also fatigue, dizziness but probably no observable impairment of reaction time or coordination; over 750 mg/m^3 has caused symptoms similar to drunkenness, numbness, and mild nausea; and over 1875 mg/m^3 has caused mental confusion, staggering gait, incoordination, lack of self-control and nervousness. Dose levels of 37500 mg/m^3 and higher are associated with narcosis and can results in unconsciousness and death within a few minutes. Slight eye irritation may start at 1125 mg/m^3 during extremely short exposure (3 to 5 minutes); and at 375 or 562 mg/m^3 during longer exposures (6 to 7 hours). Repeated or prolonged contact may cause dermatitis (red, itchy, dry skin) because of its defatting action [11].

2.3. Health hazards of xylene

The main effect of inhaling xylene vapour is depression of the CNS, with symptoms such as headache, dizziness, nausea and vomiting. The psychophysiological tests have shown no effects up to 300 mg/m^3 (70 ppm) [12] exposed for 4 hours. Volunteers have tolerated 435 mg/m^3, but higher concentrations become objectionable [13]. Exposures estimated at 3000-3045 mg/m^3 have caused dizziness, nausea and vomiting. Xylene vapour becomes irritating at relatively high levels. Eye irritation has been reported exposure to 2000 or 3000 mg/m^3 of xylene for 15 minutes. Extremely high concentrations (approximately 43000 mg/m^3) may cause incoordination, loss of consciousness, respiratory failure and death. In some cases, a potentially fatal accumulation of fluid in the lungs (pulmonary oedema) may result. Symptoms of pulmonary oedema, such as shortness of breath and difficulty breathing, may be delayed several hours after exposure. However, these effects are rarely seen since xylene is irritating and identifiable by odour at much lower concentrations [14].

2.4. Health hazards of phenol

Phenol is toxic [15]: inhalation, ingestion or skin contact with material may cause severe injury or death. Contact with molten substance may cause severe burns to skin and eyes. Colourless to light-pink, crystalline solid with a sweet, acrid odour. Phenol liquefies by mixing with about 8% water [16]. Upon heating, toxic fumes are formed. The solution in water is a weak acid. Reacts with oxidants causing fire and explosion hazard. The substance can be absorbed into the body rapidly by inhalation of its vapour, through the skin and by ingestion. A harmful contamination of the air will be reached rather slowly on evaporation of this substance at 20°C. The substance and the vapour are corrosive to the eyes, the skin and the respiratory tract. Inhalation of vapour may cause lung oedema. The substance may cause effects on the central nervous system, heart and kidneys, resulting in convulsions, coma, cardiac disorders respiratory failure, collapse. Exposure may result in death [17]. The effects may be delayed. Medical observation is indicated [18]. The symptoms of lung oedema often do not become manifest until a few hours have passed and they are aggravated by physical effort. Rest and medical observation are therefore essential. Immediate administration of an appropriate spray by a doctor or a person authorized by him/her should be considered.

III. Material and Methods

Shale fuel oil was collected from the local boiler-house in a small Estonian town, where the workers are in contact with fuel every day, when they have to clean the injector. The fuel temperature is around 70 ^{0}C and VOCs (Volatile Organic Compounds) emit from the fuel better and the smell can disperse over the whole boiler plant.

TABLE 1

Properties of shale fuel oil [19]

Quality characteristics of goods	Facts	Norms
Flash point (^{0}C)	Min 61	68
Freezing point (^{0}C)	Max - 15	-17
Sulphur (%) content	Max 0.8	0.61
Density at 15 ^{0}C (kg/m^3)	Not measured	1005.4
Moving viscosity at 80 (^{0}C)	Max 2.8	2.49
Ash (%)	Max 0.1	0.03
Water (%)	Max 1.0	0.1

The properties of the used shale fuel oil VKG D EE 10528765 TS 34:2011 are given in Table 1. In comparison to similar petroleum-based fuels, the shale fuel oil is characterised by its low viscosity and low sulphur content.

Chromatography of gases has been used as the main determination method while a lot of complex organic compounds are created in the production and handling processes of shale fuel oil. The gas chromatography-mass spectrometry (GC-MS) is the technique, where the gas chromatograph is used to separate different compounds. This stream of separated compounds is fed online into the ion source, a metallic filament to which voltage is applied. This filament emits electrons, which ionize the compounds. The ions can then further fragment, yielding predictable patterns. Intact ions and fragments pass into the mass spectrometer's analyser and are eventually detected [20]. The most common type of mass spectrometer (MS) associated with a gas chromatograph (GC) is the quadruple mass spectrometer. After the molecules travel the length of the column, pass through the transfer line and enter into the mass spectrometer they are ionized by various methods with typically only one method being used at any given time. Once the sample is fragmented it will then be detected, usually by an electron multiplier diode, which essentially turns the ionized mass fragment into an electrical signal that is then detected. The most common data representation is the mass spectrum. Certain types of mass spectrometry data are best represented as a mass chromatogram. Usually the first strategy for identifying an unknown compound is to compare its experimental mass spectrum against a library of mass spectra. The samples are thermo-stated at various temperatures in the range 40^0C – 60^0C for 15 min prior to headspace sampling. The GC temperature is programmed from 30^0C (5 min isothermal) to 200^0C (5 min) at a rate of 20^0C/min. Analysis is completed in 10 min. As the parallel analysing method, Dräger tubes (the express method) are used for determining the concentration of benzene (C_6H_6), phenols (C_6H_5-OH), xylene ($C_6H_4(CH_3)_2$) and toluene ($C_6H_5CH_3$). Determination principles and used Dräger tubes and ranges are given in Table 2.

The study includes the following activities**:**

1. To connect risk levels and health complaints, the flexible risk assessment method worked out by the authors in 2002 (Fig. 1, [21]) is used. The method is based on two-step model that could be enlarged to a six-step model, and uses (no/yes) or (corresponds to the norms/does not correspond to the norms) principle. In this study, the five-step simple/flexible risk assessment method is used. The motivation to use five risk levels is derived from BS 8800:2004 standard, which also recommends five risk levels and is therefore familiar and easy to understand to employers and occupational health and safety specialists.

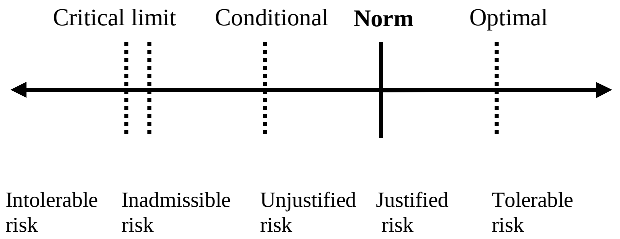

Fig. 1. Five-step flexible risk assessment method.

2. The criteria for risk levels of occupational hazards were derived from regulative norms, standards, directives and scientific literature.

3. To describe the main impact of chemicals on workers' health, the European Union's Risk-phrases (R-phrases) of chemicals were used [22]. Chemicals that were present in the examined process include toluene (R11, R38, R48/20, R63, R65, R67), xylene (R10, R20/21, R38), phenol (R34, R24/25) and benzene (R11, R45, R48, R23/24/25. To perform the measurements of occupational hazards, the following standard methods were used: ISO 7726:1998 "Thermal environments – Instruments and methods for measuring physical quantities"; EN 482:1994 "Workplace atmospheres – General requirements for the performance of procedures for the measurement of chemical agents"; EN 689:1996 "Workplace atmospheres – Guidance for the assessment of exposure by inhalation to chemical agents for comparison with limit values and measurement strategy"; EVS-EN 481:1999 "Workplace atmospheres- Size fraction definitions for measurement of airborne particles"; EN ISO 10882-2:2001 "Health and safety in welding and allied processes- Sampling of airborne particles and gases in the operator's breathing zone – Part 1: Sampling of airborne particles"; EVS-EN 1231:1999 "Workplace atmospheres – Short term detector tube measurement systems – Requirements and test methods"; WCB method 1150:1998 "Particulates (total) in air" and EN 15251:2007 "Indoor environmental input parameters for design and assessment of energy performance of buildings addressing indoor air quality, thermal environment, lighting and acoustics".

The parameters of indoor climate were measured with TESTO 435-2 (air temperature, relative humidity and air velocity) in 4 points of the workroom (8 if the surface area was over 100 m^2), at a level of 1.0 metre. Triplicate readings were recorded for each measurement and the average was presented. Chemicals were measured with the express method using the Dräger-Accuro Gas Detection Pump and the indicator tubes (specific for each chemical measured). The number of pumping was determined by the express method, e.g. for toluene 2 or 10 times (depending on the range of measurement), followed by the change of the colour of the indicate tube that detected the amount of the examined chemical in the air of the work environment. Three similar measurements were performed and the average presented.

Two types of medium fraction fuels were investigated: shale fuel oil and usual petroleum-based oil.

A. Results

The data on microclimate on the day of the measurements in the boiler-house were as follows: air temperature 20^0C; air humidity 45.5%; air velocity 0.5 m/s.

The most hazardous component in the work area is benzene (Table 3), the concentration in the worker's breathing zone was 3.2 mg/ m^3 (exposure limit= 1.5 mg/ m^3). Benzene is carcinogenic and it has to be removed from the work environment. Benzene was found both in petroleum-based fuel and shale fuel oil. The other chemicals found in the work environment (using the shale oil based fuel) over the limits were phenols. The petroleum-based fuel gave high concentration for xylene, toluene and phenols. So the shale fuel oil is safer for use. The sulphur containing components were not found in the medium fraction of shale oil. The risk assessment of benzene is shown in Fig.1. The irritating effects are given in the Fig.1, but the substance (benzene) has also the neurotoxic effects. The other measured substances (xylene, toluene, phenols) are not carcinogenic, but have upper pulmonary irritations and the risk assessment model has been worked out for all found in the air chemicals.

TABLE 2

DETERMINATION PRINCIPLES OF CHEMICALS, THE DRÄGER TUBES DETERMINATION RANGES

Reaction principle	Dräger tubes	Determination range	Colour change of adsorbent
$2\ C_6H_6 + HCHO = C_6H_6\text{-}CH_2\text{-}C_6H_6 + H_2O$ $C_6H_5\text{-}CH_2\text{-}C_6H_5 + H_2SO_4 \rightarrow$ p-chinoic compound	Benzene 0.5/c	0.5 to 10 ppm	from white to brownish-yellow
$C_6H_5OH + Ce(SO_4)_2 + H_2SO_4 \rightarrow$ brown grey reaction product	Phenol tubes 1/b	1 to 20 ppm	from yellow to brown grey
$C_6H_5CH_3 + I_2O_5 + H_2SO_4 \rightarrow I_2$	Toluene tubes 5/b	50 to 300 ppm; 5 to 80 ppm	from white to pale brown
$C_6H_4(CH_3)_2 + HCHO + H_2SO_4 \rightarrow$ quinoid reaction product	Xylene tubes 10/a	10 to 400 ppm	from white to red brown

TABLE 3

CONCENTRATIONS AND EXPOSURE LIMITS OF DIFFERENT CHEMICALS FROM FUELS IN THE AIR OF THE WORK ENVIRONMENT

Fuel	Chemicals, ppm; U=10…30%	Chemicals, mg/m^3	Exposure limit, mg/m^3
Individual boiler (petroleum-based fuel)	benzene- 1.0	3.2	1.5
	toluene- 300.0	1128.0	192.0
	xylene- 60.0	260.4	200.0
	phenol- 20.0	76.0	8.0
Commercial Boiler (shale fuel oil)	benzene- 1.0	3.2	1.5
	toluene- 6.0	23.0	192.0
	xylene- 8.0	35.0	200.0
	phenol- 9.0	34.0	8.0

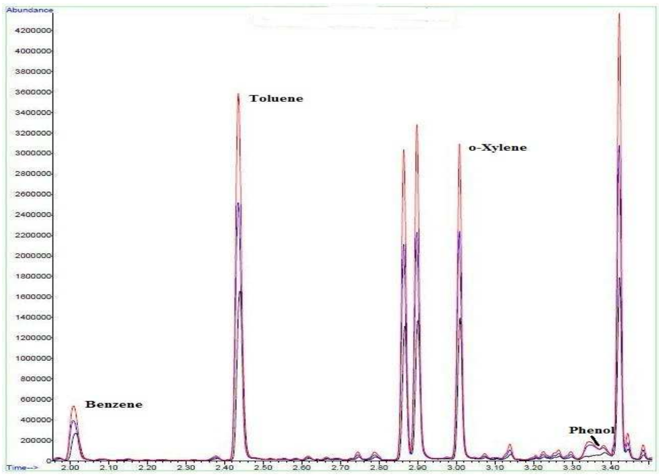

Fig. 2. Mass-spectrum of shale oil.

IV. MODELLING THE CONNECTIONS BETWEEN THE HAZARDS AND THE HEALTH DISTURBANCES

Considering data from scientific literature (case reports, occupational studies, and studies on volunteers), international standards (EVS-EN 481:1999; EVS-EN ISO 10882-2:2001) and regulative norms for chemicals in the work environment air [23] and using the flexible risk assessment method [21], the connections between risk levels and health complaints of selected chemicals have been determined.

The schemes are developed by the chemical ability to cause typical occupational disease such as cancer, short-term high risk effects, nervous system disturbances, respiratory effects, hematologic disturbances etc. as classified in OSHA Instructions [24] and is specific for each risk group (20 groups in total, 1 representing the most severe health effects). Table 5 presents the essential data of investigated four chemicals (such as odour threshold, exposure limit and IDLH value) to determine the risk levels [25], [26]. Odour threshold is an important factor to consider in risk assessment model as the hypersensitivity towards chemicals odours may be distracting and interfere with job performance and safety or induce anosmia (i.e., feeling ill from the odour of xenobiotic chemicals) [21]. Odour threshold is used as the 'optimal limit' in the current scheme.

Worker exposure concentration is an estimate of the chemical concentration that is potentially inhaled by the workers in the workplace. Occupational exposure limits [23] are specifications for the maximum airborne concentration of substances, averaged over a reference time period (in our case 8-h shift) in workplace air and are used as the 'norm' in the current scheme. They have been the primary expression of workplace risk management expectations and are suitable to divide the acceptable and unacceptable risk area (e.g. green and red area in the scheme). The 'conditional limit' is determined using the highest exposure value, which is not associated with any adverse symptoms, yet, derived from toxicological profiles.

For the 'critical limit', half of the IDLH (immediately dangerous to life or health concentration) values are used. The purpose for establishing IDLH was to determine a concentration from which a worker could escape without injury or without irreversible health effects in the event of respiratory protection equipment failure and a concentration above which only "highly reliable" respirators would be required. The IDLH values have been determined considering the toxicity data of a chemical and applying suitable safety factors [24].

TABLE 4

ODOUR THRESHOLDS, EXPOSURE LIMITS, LETHAL CONCENTRATIONS OF INVESTIGATED GASES

Hydrocarbon	Odour threshold, mg/m^3 (OSHA, 2008)	Exposure limit, mg/m^3 (Resolution, 2001)	IDLH, mg/m^3 (NIOSH, 1994)
Benzene	5	1.5	1600
Toluene	11.1	192	1880
o-Xylene	4.9	200	3906
Phenol	19	8.0	950

The five-step flexible risk assessment model, where the relationship between exposure concentration and potential health impairment is presented, is shown in Fig. 3. The occupational illness stages are developed using statistical data of diagnoses of occupational diseases by occupational health doctors. In the case of benzene, xylene, toluene and phenol, the main health impairments are divided into two different groups - irritating and neurotoxic effects.

According to the proposed scheme, the exposure to toluene and xylene poses justified risk (risk level II), benzene and phenol unjustified risk (risk level III). Without any additional control measures applied, the risk for occupational diseases caused by these chemicals is significant.

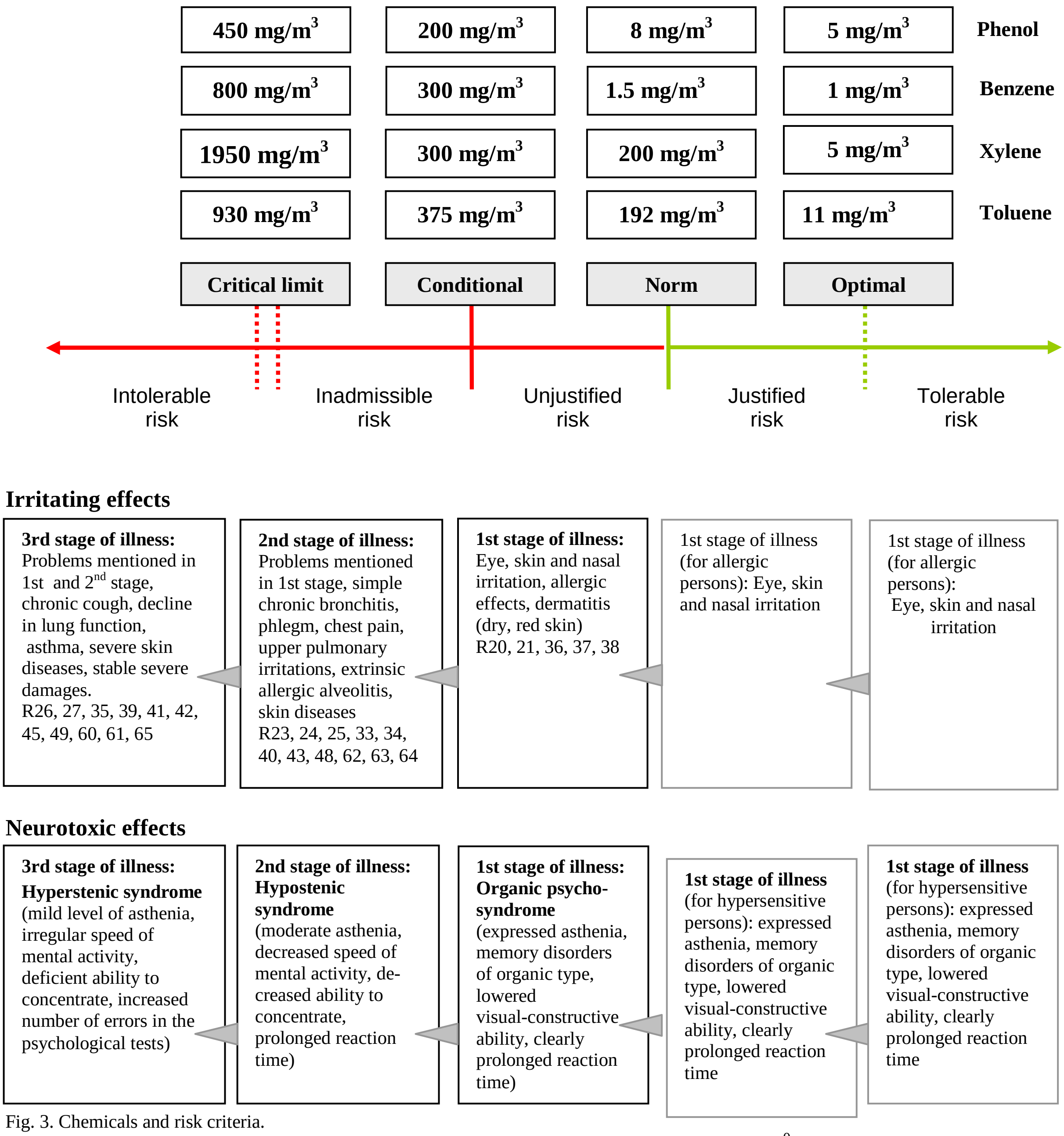

Fig. 3. Chemicals and risk criteria.

VI. Conclusions

Based on the study, the following conclusions can be drawn:

1. The dangerous VOCs (Volatile Organic Compounds) are evaporating from the shale fuel oil and will spread very likely to the ambient work environment at temperatures 40 – 60 ^{0}C in a short time. As shale fuel oil is kept in big tanks (4000 l) at temperature 30^{0}C, the VOCs can emit to the outdoor environment as well, especially in summer time.
2. The shale fuel oil has specific smell caused by sulphur components but it is difficult to designate them in the vapour phase.
3. Shale fuel oil contains benzene and this chemical is classified as carcinogen to humans.
4. Assessing chemical risk with flexible risk assessment method, the attempt to provide coherent guidance through targeting necessary information for small and medium size

enterprises to manage chemical risks and track performance more effectively. It is an alternative method to support companies in fulfilling governmental legislation of handling chemicals in occupational settings. Since the method has been worked out to assess other occupational hazards as well, it keeps a consistent manner for approaching hazards in the workplace.

5. The method is suitable for enterprises processing materials or handling chemicals in some stages, but cannot be applied for chemical plants where several other factors should be taken into account while assessing the risks for safety, health and environment. The risk of major hazards is not covered by flexible risk assessment method.

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