HEALTH RISK FROM EXPOSURE TO HYDROGEN SULPHIDE GENERATED BY RECLAMATION ACTIVITIES IN THE MYDLOVARY AREA

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Reclamation activities at the area of former uranium ore processing plant situated in the South Bohemian Region lead to emissions of hydrogen sulphide. Emissions were generated in the reclaimed impoundment and started being perceived as strong unpleasant smell by citizens of the nearby Mydlovary village during 2017. In order to identify the source of smell and to evaluate risks to human health from the exposure, the atmogeochemical survey together with measurements of the outdoor air were conducted directly at the reclaimed area, at its boundary and inside the Mydlovary village. The source of hydrogen sulphide emissions was identified in western part of currently reclaimed lagoon K IV/R. Based on the results measured calculations of noncarcinogenic human health risk were performed showing relatively low values of hazard quotient for hydrogen sulphide for the village territory. Further studies concerning the source of the hydrogen sulphide inside the lagoon were drawn.

Keywords: reclamation, human health risk, hydrogen sulphide, air pollution

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1. Introduction

Uranium ore processing plant MAPE (an acronym from MAgnesium PErchlorate) was situated in the South Bohemian Region, close to Mydlovary, Zahájí, Olešník, Nákří and Dívčice villages. Mydlovary village is the closest one to the former MAPE territory. The plant was in operation from 1962 to 1991. After it had been closed down a number of tailings impoundments from both acidic and alkaline leaching processes remained. Overall, 35.8 million tons of sludge occupied the area of 2.85 km2 situated to former Svatopluk lignite mine [1]. Reclamation activities for tailings impoundments started more than 20 years ago and are still ongoing, performed by the state company Diamo [2, 3]. For some of the sludge lagoons the work has already been finished, for the others it is still ongoing or planned. The residues from uranium mining and processing belong generally to priority environmental issues for both national and EU institutions [4].

Mydlovary village (311 inhabitants) is situated a few hundred meters from the south-western edge of the impoundments area. In 2017 an unpleasant rotten smell originating obviously within the impoundments was first detected in the village. Detailed inspection showed that the origin of the smell was situated in the K IV/R lagoon (Figure 1) where reclamation activities took place at that time. Such a smell had never been noticed during reclamation work before. The village inhabitants initiated an investigation, which suggested that the smell might mostly be related to hydrogen sulphide and its intensity was changeable, depending on meteorological conditions, such as the velocity and direction of the wind. The smell could be felt outside as well as inside living apartments.

Two relevant documents were provided to the Mydlovary inhabitants as far as the occurrence of hydrogen sulphide at the village territory is concerned. The first one followed from the air quality measurement ordered by the Diamo Co. which resulted in the hydrogen sulphide air concentrations 2.7 - 4.7 mg.m^{-3} reported for the K IV/R lagoon area [5]. The second one summarized the investigation of the Czech Environmental Inspectorate, which monitored the smelling substances in air through the olfactometry technique and reported the values of 1367; 2001; 1742 OUE.m^{-3} for the three sampling points situated at the lagoon area. The value of 10 OUE.m^{-3} was then suggested as the acceptable limit for the lagoon boundary [6].

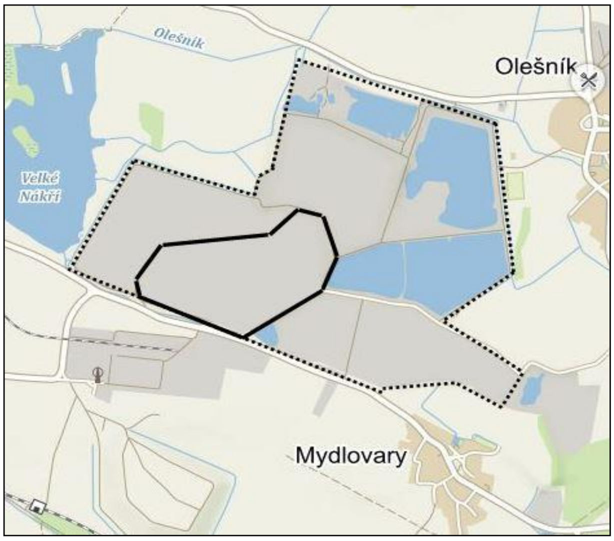

Figure 1: General location of MAPE impoundments area with sludge lagoon K IV/R

Reclamation works carried out at the K IV/R lagoon included depositions of different solid materials, such as demolition waste, coal combustion residuals or waste tyres [2]. Demolition waste partly consisted of gypsum drywall. Tyres served here as a framework that was filled with other reclamation materials [3]. The final surface of the reclaimed lagoon is planned to be sealed with clay and covered with biological layer (that includes soil layer and grass), thus forming a visually attractive landscape. The reclamation materials applied here are generally supposed to be inert towards the substances already present inside the lagoon and no chemical reactions should appear.

In response to the inquiry of the Mydlovary inhabitants Diamo company started using lime at the reclamation site, mixing it with wastewater to increase pH [7], and suggested that the unpleasant smell that caused the complaints will disappear with the end of reclamation works on K IV/R impoundment. As reported by the citizens, the smell became weaker after lime started to be applied.

Hydrogen sulphide is a colourless gas which generally may enter the atmosphere both from natural sources and from human activities. Only about 10% of the total global emissions of this compound are of anthropogenic origin. Hydrogen sulphide has an odour detection threshold of about 0.2 - 2.0 μg.m^{-3} depending on the purity and with considerable individual variability. Its characteristic smell of rotten eggs appears at concentrations 3-4 times higher than the odour threshold. However, at concentrations higher than ~ 150 mg.m^{-3}, individuals may not detect hydrogen sulphide odour due to olfactory paralysis. Thus the odour can no longer be recognized as a warning signal. Hydrogen sulphide causes odour nuisance at concentrations far below those that cause acute health hazards. On the basis of the scientific literature, it is not possible to state a specific concentration of hydrogen sulphide at which odour nuisance starts to appear. Half-hour average concentrations exceeding 7 μg.m^{-3} are likely to produce substantial complaints among persons exposed [8].

Acute forms of hydrogen sulphide intoxication are mainly related to the effects on nervous system. At concentrations of 15 mg.m^{-3} and above, hydrogen sulphide causes conjunctival irritation. Hydrogen sulphide affects the sensory nerves in the conjunctivae, so that pain is diminished rapidly and the tissue damage is greater. Serious eye damage is caused by a concentration of 70 mg.m^{-3}. At higher concentrations, respiratory irritation is the predominant symptom, and at a concentration of around 400 mg.m^{-3} there is a risk of pulmonary oedema. At even higher concentrations there is strong stimulation of the central nervous system, with hyperpnoea leading to apnoea, convulsions, unconsciousness, and death. At concentrations of over 1400 mg.m^{-3} there is immediate collapse. In fatal human intoxication cases, brain oedema, degeneration and necrosis of the cerebral cortex and the basal ganglia have been observed [8, 9, 10]. Fatal cases caused by hydrogen sulphide are rare, few of them have however been reported for the Czech Republic [11, 12, 15].

The hazards caused by high concentrations of hydrogen sulphide are relatively well known, but information on human exposure to low concentrations is scanty. Most probably, at concentrations below 1.5 mg.m^{-3}, even in exposure for longer periods, there are very few detectable health hazards in the toxicological sense. The malodorous property of hydrogen sulphide is a source of annoyance for a large proportion of the general population at concentrations below 1.5 mg.m^{-3}, but from the existing data it cannot be concluded whether any health effects result [8]. In order to avoid substantial complaints about odour annoyance among the exposed population, hydrogen sulphide concentrations should not be allowed to exceed 7 μg/m3, with a half-hour averaging period.

Hydrogen sulphide might not necessarily be the only chemical substance responsible for the smell appearing at the Mydlovary area. Solid reclamation materials are typically quite complex and another smelling substances may generally originate under anaerobic conditions, such as carbon disulphide, carbonyl sulphide, dimethyl sulphide, mercaptanes and thiophenes [16, 17]

Taking into account the above presented introduction, there existed a strong need to monitor the occurrence of hydrogen sulphide (possibly another smelling substances) in the Mydlovary village as well as at the K IV/R lagoon area which was considered as a probable source of hydrogen sulphide. There was further a question about the level of human health hazard which might follow from the hydrogen sulphide concentration measured.

Thus the goal of this work is to perform a set of the air (including subsurface air) quality measurements and interpret the data collected by means of the human health risk assessment procedure The US EPA guideline for inhalation risk assessment was applied to this purpose here [13].

2. Experimental

2.1. Air sampling

Three different air sampling techniques were employed in this work. The first one was used for preliminary monitoring at the K IV/R lagoon and included simple sampling into polypropylene bags. The second one was applied for long-termed air sampling at the Mydlovary village territory. The third one was applied for identification of the hydrogen sulphide source at the area of the K IV/R lagoon and was based on the atmogeochemical monitoring.

Preliminary monitoring at the K IV/R lagoon was carried out at 21.09.2017 and was aimed to quantify the actual hydrogen sulphide concentration at the lagoon boundaries as well as to detect other possible smelling substances. Partial air volumes (taken in regular intervals with a 100-mL polyethylene syringe at the lagoon perimeter) were introduced into a 5-L polypropylene sampling bag RESTEC LR4150-24D whose inner surface was inertized towards hydrogen sulphide. The bag volume was filled up within ~30 minutes, the sampling was repeated twice. Analyses of the two bags were performed 20 hours after sampling.

The long-termed sampling runs at the Mydlovary village were carried out within 2. 10. - 14. 10. 2017 (275 hours in total) and within 3. 11. - 12. 11. 2017 (228 hours in total). An absorption system was used here based on two absorption bottles connected in series, each one filled up with 300 ml of 0.1 M NaOH solution. Laboratory air pump set up to the flow rate of 0.03 m3.h-1 was used to drive the sampled air into the bottles. The absorption system was placed to house of registration number Mydlovary 109 and situated in the garden pergola, i.e. protected against rain but exposed to outdoor conditions. Analysis of the liquid sample was carried out two days after sampling.

The atmogeochemical monitoring was based on subsurface air sampling which was carried out by the sampling set shown at Figure 2. Steel hollow sampling tube was hammered into the subsurface to the depth of about 0.5 - 0.7 m and sealed in its upper part by alluminium cone. The tube was then connected to the Multitec 540 device (Hermann Sewerin GmbH) equipped with detector of hydrogen sulphide. Atmogeochemical monitoring was carried out in a preliminary sequence first which was followed by detailed mapping. Preliminary atmogeochemical search (28.03.2018 and 21.5.2018) was aimed to get approximate knowledge on hydrogen sulphide distribution and concentrations in the subsurface air. Detailed search (14.6.2018) was performed to provide detail concentration maps on the K IV/R lagoon area.

Figure 2: Sampling set for atmogeochemical survey

2.2. Air analysis

Samples of the air taken at the lagoon perimeter were analysed by gas chromatography unit Agilent 7890A equipped with chemiluminescence detector. The air from sampling bag was injected directly to the unit by means of 20-mL gastight syringe. Each sampling bag was analysed four times and the partial results were averaged.

The alkaline aqueous solutions in the absorption bottles were acidified by sulphuric acid to transfer the sodium sulfide to hydrogen sulphide, which was then stripped out to sampling bag RESTEC. The following instrumental analysis was the same as described above.

3. Results and discussion

Duplicated air sampling carried out within preliminary investigation at the perimeter of the reclaimed K IV/R lagoon resulted in hydrogen sulphide concentration 2.8 mg.m^{-3} for the first sampling bag and 2.9 mg.m^{-3} for the second sampling bag. These results well correspond to the conclusions [5] of the prior monitoring completed in summer 2017 by the Diamo company which for the same sampling area reported the concentrations moving within the range 2.72 - 4.72 mg.m^{-3}. The data clearly confirmed that the air in the close proximity of the lagoon was over a long period polluted with hydrogen sulphide whose concentrations generally ranged within the units of mg.m^{-3}. The analyses of the two air samples with the Agilent 7890A unit did not indicate measurable amounts of other substances besides hydrogen sulphide. Thus hydrogen sulphide was considered as the only pollutant of interest.

The long-termed continuous sampling situated directly to the village territory showed the averaged hydrogen sulphide concentration 0.09 μg.m^{-3} for the first period (October 2017), while the concentration following from the second sampling period (November 2017) was below the detection limit (<0.01 μg.m^{-3}). The hydrogen sulphide concentration to which village inhabitants were exposed in October 2017 was in two orders of magnitude lower compared with those measured at the lagoon perimeter. It should be noted here that the sampling was carried out under generally windy weather. The intensity of smell, according to the village inhabitants, was relatively low in this time.

A preliminary stage of the atmogeochemical monitoring identified measurable concentrations of hydrogen sulphide in the subsurface air (Multitec 540 detection limit = 1.0 ppm (1.5 mg.m^{-3})) only in a western part of the lagoon. The detailed mapping including 44 measurement points was thus focused mainly to this section. The experimental results were processed through the program Surfer, which is a contouring and surface mapping software. As shown in Figure 3 there was only one identifiable centre from which hydrogen sulphide obviously escaped to the lagoon surroundings which most probably indicated the existence of some preferable pathway for hydrogen sulphide escaping. This centre was situated about 150 m from the western edge of the lagoon and the hydrogen sulphide concentration in its midpoint reached up to 3000 mg.m^{-3}. However, not more than about 15-20 meters away from the midpoint the hydrogen sulphide concentration decreased below 1000 mg.m^{-3} and further rapidly lowered with distance. The area with hydrogen sulphide detectable concentrations (i.e. higher than 1.5 mg.m^{-3}) was approximatelly 2000 m2.

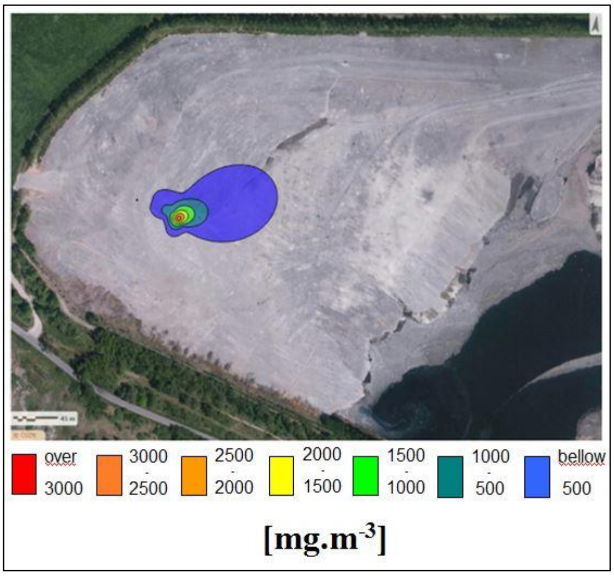

Figure 3: Graphical interpretation of detailed atmogeochemical exploration of the K IV/R lagoon (performed on 14. 06. 2018). The ranges of hydrogen sulphide concentrations indicated by coloured scale

The primary interpretation of the hydrogen sulphide concentration measured at the village area may consist in comparing them with relevant limiting values. As already mentioned in the introductory part, there exist no legal enactments in the Czech Republic, which would directly provide the limiting values for hydrogen sulphide occurrence in the outdoor atmosphere. The only limiting values clearly supported by national legislation are those for occupational exposition (permissible exposure limit PEL = 7 $mg.m^{-3}$, maximum permissible concentration NPK-P = 14 $mg.m^{-3}$). It should be however mentioned here that the Czech National Health Institute provided a list of the reference concentrations [14], which might be considered as recommended limits for outdoor air - the value, stated here for hydrogen sulphide is 150 $\mu g.m^{-3}$. It is however directly noted in the list that this hydrogen sulphide reference concentration does not ensure protection against smell. The hydrogen sulphide concentration of 7 $\mu g.m^{-3}$ is stated here as a limiting value for smell. Thus considering the above-specified limits for occupational exposition as well as the reference concentration [14], we may conclude that neither workers moving at the lagoon surface nor the Mydlovary inhabitants are exposed to over-limit hydrogen sulphide concentrations. The values reported for lagoon perimeter (lower units of $mg.m^{-3}$) are satisfactory for occupational hazard and the hydrogen sulphide concentrations measured directly in village (0.09 $\mu g.m^{-3}$) is far below the suggested long-term smell limit 7 $\mu g.m^{-3}$.

The measured concentrations of hydrogen sulphide may further be compared with the hydrogen sulphide sensory effects and its toxicological limits as summarized in Figure 4.

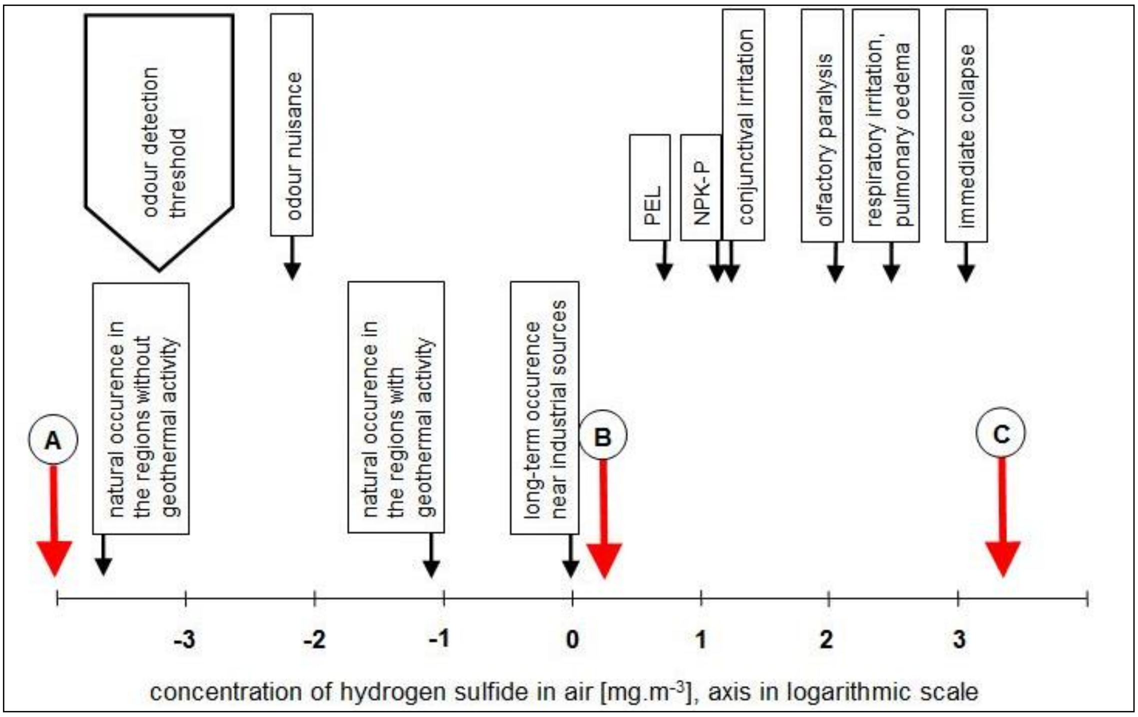

Figure 4: Hydrogen sulphide sensory effects and its toxicological limits (red arrow (A): air hydrogen sulphide concentration measured for long-term sampling at the Mydlovary village area; red arrow (B): air hydrogen sulphide concentration measured for lagoon perimeter; red arrow (C): the highest hydrogen sulphide concentration measured in the subsurface air at the lagoon K IV/R)

In this relation, it is important that the hydrogen sulphide concentrations detected for village territory do not exceed natural air occurrence for the regions without geothermal activity.

Irrespective of absence of the directly applicable legal enactments, the influence of chemicals to human health may be assessed by means of the risk assessment procedures, which are widely supported by methodological guidelines.

The chemical substances may generally bring two types of risks towards human population - carcinogenic and non-carcinogenic. The assessment of human health hazard following from the occurrence of a chemical substance is typically completed for a specific scenario - here the long-time exposure of the Mydlovary inhabitants to low concentration of hydrogen sulphide. No other toxic substances are considered here and inhalation exposure may be identified as the only route through which hydrogen sulphide enters the human body. Hydrogen sulphide has not been shown to cause cancer in humans, so the carcinogenic risk may be excluded here.

The non-carcinogenic human health hazard assessment is traditionally based on the Hazard Quotient (HQ) concept, which is defined as the ratio of the potential exposure to a chemical substance to the level at which no adverse effects are expected. If the Hazard Quotient is calculated to be less than 1, then no adverse health effects are expected as a result of exposure. If the Hazard Quotient is greater than 1, then adverse health effects are possible.

Hazard Quotient for the inhalation exposure to hydrogen sulphide was calculated from the following formula:

Inhalation HQ=EC/(RfC x CF)

where:
HQ – hazard quotient (dimensionless),
EC – exposure concentration ($\mu g.m^{-3}$)
RfC – inhalation reference concentration ($mg.m^{-3}$)
CF – conversion factor, 1000 (µg.mg-1)

The U. S. EPA guideline [13] has defined chronic inhalation reference concentration (RfC) for hydrogen sulphide to be 0.002 $mg.m^{-3}$. Thus for the hydrogen sulphide concentration identified directly in the village (0.09 $\mu g.m^{-3}$) the value of HQ is calculated to be 0.045. For the hydrogen sulphide concentration identified for the K IV/R lagoon perimeter (2800 $\mu g.m^{-3}$; 2900 $\mu g.m^{-3}$) the related values of HQ are 1400; 1450 respectively. Since these HQ values are relatively far from the boundary value 1, the basic interpretation is relatively simple. The value 0.045 calculated for the village territory does not indicate the occurrence of adverse health effects for the inhabitants. The HQ values calculated for the air sampled at the lagoon are, on the other hand, quite high and indicate potential for non-carcinogenic effects to the people exposed. In other words, the 275 hours sampling carried out directly at the village territory within 2.10. - 14.10.2017 showed very low averaged concentration of hydrogen sulphide, even lower than odour detection threshold or naturally occurring hydrogen sulphide concentrations (see Figure 4). Much higher hydrogen sulphide concentrations - units of $mg.m^{-3}$ - detectable at the K IV/R lagoon perimeter may be considered as potentially hazardous. On the other hand, there are no residents at the lagoon territory, only workers to whom the legal limits for occupational exposition apply.

The concept of the Hazard Quotient is not directly implemented in the Czech environmental legislation. Thus the values higher than 1 (even significantly higher) do not automatically bring the need to start remedial activities at the impacted area. There however exists a well established procedure widely applied by state administration in the assessment of subsurface contamination. The decision to remediate the contaminated subsurface must traditionally be supported by the conclusions of risk assessment report where hazard quotient presents one of the important parameters analysed. So irrespective of the absence of directly applicable legal enactment the hydrogen sulphide presence in the Mydlovary village might be interpreted through the guidelines for the risk assessment process. Such an assessment would be a strong decision tool for the relevant state authorities, such as for example Environmental Inspectorate.

Figure 4 gives a graphic representation of the variety of possible effects of hydrogen sulphide on human health in relation to its air concentrations, along with the above presented concentrations detected in the centre of the contaminated subsurface air pocket in the lagoon K IV/R, at the perimeter of the lagoon, as well as at the territory of Mydlovary village. It clearly follows from Figure 4 that no adverse effects may be expected towards the Mydlovary inhabitants in relation to the hydrogen sulphide air concentration measured in October 2017. Similarly, no disagreements were identified with the occupational exposition limits for the workers moving inside the lagoon territory. Thus, the future attention should mainly be directed to the high subsurface air concentrations, which might indicate the existence of undesirable chemical and/or microbiological processes.

4. Conclusions

Atmogeochemical monitoring carried out at the area of the reclaimed K IV/R lagoon identified a small hydrogen sulphide pocket in the western part of the lagoon where the subsurface hydrogen sulphide concentration reached up to 3000 $mg.m^{-3}$. The hydrogen sulphide concentration measured at the lagoon perimeter was significantly lower - less than 3.0 $mg.m^{-3}$. The duplicated long-term sampling performed at the territory of Mydlovary village showed the concentration of 0.09 $\mu g.m^{-3}$ in the first sampling run and the concentration below the detection limit for the second run. These low level actual concentration of hydrogen sulphide identified for the village territory do not imply any health risk and are comparable with natural occurence of hydrogen sulphide

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