Emission of halocarbons from an hazardous waste landfill in Italy

EMISSION OF HALOCARBONS FROM AN HAZARDOUS WASTE LANDFILL IN ITALY

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SUMMARY: Landfills are sources of fugitive volatile organic carbon (VOC) emissions, including halocarbons. The objective of this study was to evaluate the contribution of halogenated VOCs to the health risks associated with the exposure of workers operating in landfills, gathering information on the role of endogenous/exogenous sources present in anthropized areas. A hazardous waste landfill located in Turin, Italy was used as a case study. Ambient concentrations of 10 pollutants (BTEX, styrene, 1,3,5-trimethylbenzene, 1,2,4-trimethylbenzene, 1,2-dichloroethane, and 1,2-dichloropropane), measured in 10 points of the landfill area, were considered and analyzed. The data had a monthly frequency and covered two years. A cumulative health risk analysis was conducted by applying a Monte-Carlo method. The results showed that the contribution of 1,2-dichloroethane and 1,2-dichloropropane was 17.9% and 19.4% for the total risk and hazard index respectively. Benzene and ethylbenzene gave the highest contribution to the total risk (56.8% and 24.8%, respectively). In the second phase of the study, waste typologies that are possibly responsible for halocarbon emissions were investigated. Halocarbon concentration trends and waste disposal records were compared. Although further investigation is needed, some waste typologies were not excluded to contribute to halocarbon emissions, in particular sludge coming from wastewater treatment plants.

1. INTRODUCTION

Halocarbons are substances emitted by anthropogenic sources, which are commonly employed as solvents cleaners, refrigerants, and reagents in the plastic and metal industry. Long-term exposure to halocarbons has been associated with some potential health risks, in particular to some respiratory problems, such as irritation and cancer (Huang et al., 2014). Landfills may be a source of fugitive volatile compound emissions, including halocarbons (Liu et al., 2016; Wu et al., 2018).
Several studies were done on the fugitive emissions of municipal solid waste landfills, analyzing emissions, odours, and risks. In terms of local air quality, the presence of large quantities of potentially hazardous mixtures of chemicals in landfill sites close to residential populations has increasingly caused concern (Vrijheid, 2000). For this reason, a substantial number of studies on the health effects associated with landfill sites were conducted in the last years. Health risk analysis (HRA) is the consolidated methodology to evaluate citizens' and workers' exposure to pollutant emissions.
The present study was focused on the analysis of fugitive halocarbon emissions from hazardous waste landfills. The objective was to evaluate the contribution of halogenated VOCs to the cumulative

health risks associated with the exposure of workers operating in the landfill sites. The contribution of halocarbons to the total risk was compared to those of other VOCs, gathering information on the possible role of endogenous/exogenous sources present in densely anthropized areas. The Barricalla site, a hazardous waste landfill located in Turin, Italy, was used as a case study. 1,2-dichloroethane and 1,2-dichloropropane were selected as marker substances of halocarbons' presence. The present study also considered the characterization of the uncertainty related to the HRA methodology. The HRA was calculated by means of a novel approach, based on the probabilistic analysis of ambient air pollutant concentrations.

2. METHODOLOGY

The risk contribution of halocarbon emissions from hazardous waste landfills was evaluated through the application of a health risk analysis (HRA) approach, considering the exposure of possible workers operating on the site. The considered case study was the Barricalla landfill, located close to the town of Turin, northern Italy. As demonstrated by previous research activity on HRA, particular care must be addressed to the definition of the representative pollutant concentration levels, especially when exposure to multiple chemical substances is evaluated (Schuhmacher et al., 2001). Considering only the average or maximum of the observed concentrations might not be, in some cases, representative of the effective long-term exposure of workers. If an adequate number of observations is available, the analysis of the probability distribution of measured concentrations and the application of Monte-Carlo methods could provide support in this sense. For this reason, in our study, the calculations of HRA were preceded by an analysis of the concentrations of the chemical species that were measured on site. Data of the ambient concentration of pollutants recorded in 7 sampling points of the study site in the period 2016–2017 were elaborated to find the best fitting probability distribution. One distribution curve per pollutant species was defined. These curves were then used to generate large vectors of the estimated concentration values. Cumulative HRA was then calculated repeatedly using vectors of the estimated concentration values as an input, as described in the following sections. The scheme of the operating model used in this study is reported in Figure 1. More information about the methodological procedure is reported in Ravina et al. (2020).

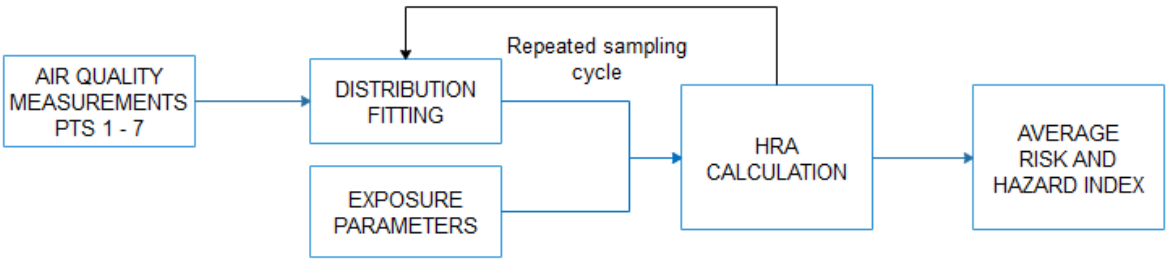

Figure 1. Scheme of the operational model for health risk analysis.

2.1. Case Study

The studied area is situated northwest of Turin, close to an industrial area and the town ring road (Figure 2). The Barricalla landfill has a comprehensive area of 150,000 m^2 divided into 5 lots. The area previously housed a gravel pit of about 600,000 m^3, used mainly for the extraction of raw materials for the construction of the Turin ring road. The Barricalla landfill was inaugurated in 1988; lots 1 and 2 have been exhausted and closed. Lot 4 and lot 3 were declared terminated in April 2017 and July 2018, respectively. Recently, the new lot 5 was built, which can accommodate 508,850 m^3 of wastes.

The site is Eco-Management and Audit Scheme (EMAS) certified and subjected to the Integrated Pollution Prevention and Control (IPPC) authorization. Generally, the wastes conferred in this landfill are industrial sludge, railway ballasts, wastes from the treatment of flue gas of steel mills, ashes from incineration, land reclamation, and wastes from treatment plants. Two different kinds of analyses are performed on waste before its disposal: an analysis on the eluate and another on the solid waste.

Figure 2. Photo of the Barricalla landfill.

Concerning the emissions into the atmosphere, measures on ambient air and landfill gas are done regularly. Ambient air monitoring is measured with a monthly frequency on 11 points (Figure 3) and includes the following compounds: 1,2-dichloroethane, benzene, 1,2-dichloropropane, toluene, ethylbenzene, meta- and para- xylene, styrene, ortho-xylene, 1,2,4-trimethylbenzene, and 1,3,5-trimethylbenzene. The meteorology of this area is characterized by low winds, in particular during summer and winter. In this area, during the cold season, pollutant dispersion is mainly regulated by local breeze regimens and soil heat-induced turbulence, which is minimum from December to February. Precipitations are minimum in January.

This study considered all the pollutants monitored on the site, with a particular focus on 1,2-dichloroethane and 1,2-dichloropropane.

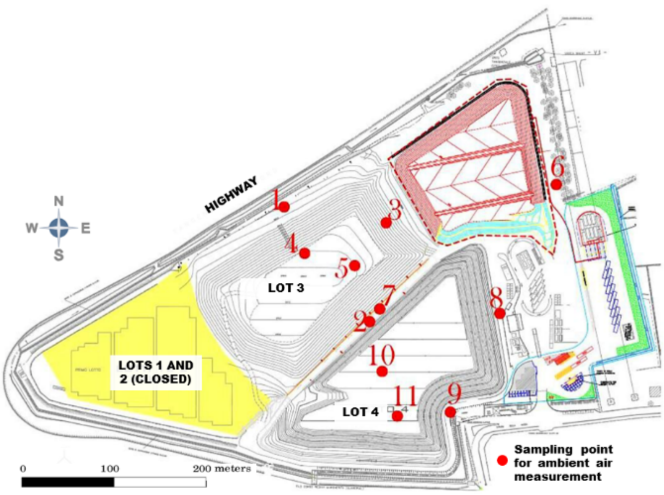

Figure 3. Location of sampling points for ambient air monitoring.

2.2. Calculation Approach

To define the most representative values of the pollutant concentration to which landfill workers are exposed, the data collected from the ambient air monitoring systems were analyzed to define their probability distribution. These data were analyzed with the use of the Distribution Fitter tool of the Matlab software (Mathworks Inc.). To evaluate the best fit, the principle of maximum log-likelihood estimates was adopted. One distribution was obtained for each pollutant. These data were used to calculate risk and hazard index (HI) by applying a Monte-Carlo method. A Matlab script was generated to calculate the single and cumulative risk and hazard index based on standard HRA methodologies.

3. RESULTS

Ambient air concentrations were analyzed. It was found, for every substance, that a log-normal distribution provided the best fit on the data. For each substance, the statistical parameters (μ and σ) corresponding to the best fit, i.e., maximum log-likelihood, were also calculated. The sampling mean, standard deviation, 95th percentile, and μ and σ parameters of the corresponding log-normal distribution are reported in Table 1.

Table 1. Probability distribution parameters of the measured concentrations.

Compound	Mean (μg/m^3)	Standard Deviation (μg/m^3)	95th Percentile (μg/m^3)	Detection Limit (μg/m^3)	μ	σ
1,2-dichloroethane	0.1819	0.2896	0.4000	0.2	–1.9841	0.5863
Benzene	2.5653	1.6567	6.1000	0.2	0.7249	0.6938
1,2-dichloropropane	0.2847	0.5268	0.6000	0.2	–1.6635	0.7406
Toluene	3.5715	2.3640	8.2300	0.2	1.0641	0.6931
Ethylbenzene	2.9958	1.8443	6.5900	0.2	0.9178	0.6350
Meta Xylene and Para Xylene	4.5118	2.6380	9.7400	0.2	1.3455	0.5982
Styrene	0.3131	0.6955	0.6000	0.2	–1.5026	0.6563
Ortho Xylene	2.1012	1.2596	4.6400	0.2	0.5733	0.5936
1,3,5-trimethylbenzene	1.1500	0.5608	2.1000	0.2	0.0189	0.5128
1,2,4-trimethylbenzene	0.9458	0.6456	1.8100	0.2	–0.2193	0.5977

The results of the HRA are reported in Table 2. To estimate the effect deriving from the coexistence of more than one substance, the cumulative risk and hazardous index were calculated through the sum of the individual parameters. The commonly assumed benchmark values below which risk is considered negligible are 10^{-6} for single substances and 10^{-5} for cumulative risk. For the hazard index, a limit of 1 is considered both for single substances and mixtures (INAIL, 2014). The results show that the average cumulative risk does not exceed the benchmark value, indicating that the risk for workers is most probably negligible (average R = 7.16 10^{-6} standard deviation = 3.70 10^{-6}). As expected, the distribution of the cumulative risk values is log-normal ($\mu = -11.96 \pm 0.0014$; $\sigma = 0.446 \pm 0.0009$). This additional result shows that the benchmark value of 10^{-5} was exceeded by 16% of the simulations. Considering the relative contribution of single substances to the cumulative risk, Table 2 shows that benzene and ethylbenzene give the highest contribution to the total risk (56.8% and 24.8%, respectively). The contribution of halocarbons is 14.6% for 1,2-dichloroethane and 3.3% for 1,2-dichloropropane. Of the single substances, only benzene and ethylbenzene exceed the value of 10^{-6}.

The average cumulative HI is 0.0965 (standard deviation = 0.0315), meaning that the benchmark value is not exceeded. Additionally, the cumulative HI values are aligned on a log-normal distribution (μ = −2.386 ± 0.0009; σ = 0.306 ± 0.0006). For HI, the benchmark value of 1 is never exceeded, meaning a negligible probability of intoxication for workers. Considering the relative contribution of single substances to the cumulative HI, Table 2 shows that meta- and para-xylene and benzene give the highest contribution to the total HI (34.3% and 19.2%, respectively). The contribution of halocarbons is 5.5% for 1,2-dichloroethane and 13.9% for 1,2-dichloropropane. The threshold value of 1 is not exceeded for any of the substances.

Table 2. Results of the health risk analysis.

Compound	Exposure E = CRS·EM	SF	RfD	Risk R (Average)	Relative Contribution to Cumulative R (%)	Hazard Index HI (Average)	Relative Contribution to Cumulative HI (%)
1,2-dichloroethane	$1.02\ 10^{-5}$	$9.10\ 10^{-2}$	$2.00\ 10^{-3}$	$9.07\ 10^{-7}$	14.6	0.0050	5.5
Benzene	$1.54\ 10^{-4}$	$2.73\ 10^{-2}$	$8.57\ 10^{-3}$	$4.40\ 10^{-6}$	56.8	0.0188	19.2
1,2-dichloropropane	$1.55\ 10^{-5}$	$1.30\ 10^{-2}$	$1.14\ 10^{-3}$	$1.97\ 10^{-7}$	3.3	0.0133	13.9
Toluene	$2.08\ 10^{-4}$		1.43	0	-	0.0006	0.6
Ethylbenzene	$1.77\ 10^{-4}$	$8.75\ 10^{-3}$	$2.86\ 10^{-1}$	$1.63\ 10^{-6}$	24.8	0.0007	0.7
Meta- and Para-Xylene	$2.66\ 10^{-4}$		$2.86\ 10^{-2}$	0	-	0.0344	34.3
Styrene	$1.89\ 10^{-5}$	$1.75\ 10^{-3}$	$2.86\ 10^{-1}$	$3.00\ 10^{-8}$	0.5	0.0001	0.1
Ortho Xylene	$1.25\ 10^{-4}$		$2.86\ 10^{-2}$	0	-	0.0158	16.8
1,3,5-trimethylbenzene	$6.95\ 10^{-5}$		$5.71\ 10^{-2}$	0	-	0.0044	4.9
1,2,4-trimethylbenzene	$5.56\ 10^{-5}$		$5.71\ 10^{-2}$	0	-	0.0036	4.0
Cumulative				**7.16** 10^{-6}		**0.0965**	

4. DISCUSSION

The HRA applied to the ambient air inhalation of workers operating on the landfill site showed that the cumulative risk and hazard index were below the threshold limits indicated by current regulations. The joint contribution of 1,2-dichloroethane and 1,2-dichloropropane was 17.9% and 19.4% for the total risk and HI, respectively. The results found can be compared to other studies on MSW landfills, as no similar studies done on hazardous waste landfills were found in the bibliography. Previous research works mainly focused on aromatics. If halocarbons were considered, only a limited number of substances were included in the analysis. A study conducted on a large municipal solid waste landfill in Bejing, China calculated the health risk of VOC inhalation close to the tipping area (Wu et al., 2018). The following ranges of HI were found, depending on the period of the year: Trichloropropane, 4.9 10^{-2}; benzene, 5.5 10^{-4}–1.3 10^{-2}; and tetrachloroethylene, 1.3 10^{-2}–1.5 10^{-1}. Risk ranges were the following: Benzene, 1.3 10^{-7}–2.0 10^{-5}; and tetrachloroethylene, 9.5 10^{-7}–1.5 10^{-6}. The cumulative HI ranged between 2.5 and 5.7. The cumulative risk range was 1.0 10^{-4}–3.4 10^{-4}. Aromatics and halogenated compounds contributed the most to carcinogenic risk (79% and 21%, respectively). The cumulative HI was dominated by H_2S (67%), halocarbons (14%), and aromatics (10%). The results of benzene were similar to the average found in the present study. The cumulative risk and hazard index were around two orders of magnitude higher. The contribution of halocarbons to the cumulative risk and HI was similar. Palmiotto et al. (2014) presented an HRA of an MSW landfill located in central Italy. The cumulative cancer risk for residents living in the vicinity of the

facility (around 1 km) ranged between 2.6 10^{-9} and 3.6 10^{-8} depending on the direction from the center of the landfill. The cumulative HI ranged between 8.1 10^{-6} and 1.6 10^{-4}. These values are around two orders of magnitude lower than the present study, indicating that the risk is significantly affected by the exposure distance. The exposure to vinyl chloride monomer (VCM) indicated a specific risk and a HI range of 9.2 10^{-11}–8.8 10^{-9} and 2.0 10^{-7}–4.0 10^{-5}, respectively. Liu et al. [4] conducted an HRA of the exposure to BTEX in an MSW landfill in China at a distance of 0.5 km from the landfill borders. The result showed cumulative HI between 3.53 10^{-2} and 1.77 10^{-1} and cumulative risk between 9.23 10^{-7} and 4.63 10^{-6}. Regarding the most hazardous substances, the results were the opposite compared to the present study. HI was dominated by toluene (HI = 2.81 10^{-2}). The risk of benzene exposure was 1.59 10^{-6}, lower than ethylbenzene (3.46 10^{-6}). Like the present study, the emission rates of toluene and p+m xylene fitted the log-normal distribution. Ethylbenzene fitted a gamma distribution. In another study on a Serbian MSW landfill, a cumulative risk of one order of magnitude lower than the present was found (Petrovic et al., 2018). HCH was the only halocarbon investigated, and its specific risk was 2.28 10^{-8}.
The results presented herein show similarities and differences if compared to existing studies. Both the exposure risk and HI are, except for the Beijing case, not significant. The contribution of halocarbons to the total risk and HI is limited, and BTEX contribute the most. Nevertheless, the analysis of 1,2-dichloroethane and 1,2-dichloropropane showed that even a limited quantity of these substances contributed to increasing the cumulative risk. In fact, considering Table 1, the average concentrations of 1,2-dichloroethane and 1,2-dichloropropane were around 10 times lower than those of benzene and ethylbenzene. The differences between this and other studies may depend on different factors: Waste composition, landfill management, analysis methodology (substances considered, distance, exposure parameters), and features of the area. The methodology presented in this study improved the characterization of the uncertainty associated with HRA calculations, as it allowed definition of the site-specific most probable exposure concentrations of pollutants.

5. CONCLUSIONS

Halogenated VOCs or halocarbons are highly volatile compounds that produce negative effects on human health and contribute to the greenhouse effect. Monitoring and limiting the presence of these substances in the atmosphere is thus crucial, in particular where different types of emission sources are present. Fugitive emissions from the working face of hazardous waste landfills can include halocarbons that are originally contained in the waste. This study had a dual objective. The first was evaluating the potential contribution of halocarbons to the health risks for landfill workers. The second was the analysis of the possible waste typologies emitting halocarbons. The Barricalla site, a hazardous waste landfill close to the city of Turin, Italy, was used as a case study. In the first part of the study, a probabilistic approach was adopted to characterize the uncertainty associated with the method. In the case study analyzed, the most probable cumulative risk and hazard index were below the benchmark values. Halocarbons (1,2-dichloroethane and 1,2-dichloropropane) were not the major contributors to the total risk for the workers. Nevertheless, within the scope of the continuous improvement of the air quality in heavily anthropized areas, a deeper evaluation of the possible sources and remediation actions seems to be necessary.
From this perspective, it is recommended that further research should focus on (i) improving the traceability of the waste treatment chain and (ii) improving the waste treatment processes (partial stabilization) in a way to limit fugitive emissions.
In conclusion, in hazardous landfill sites in which up-to-date environmental management is conducted, fugitive emissions of halocarbons should not represent a hazard for the health of workers

or the nearby population. Nevertheless, in emission contexts where multiple pollution sources are present, different emerging and minor hazardous pollutants, including halocarbons, may be present. These substances may pose a risk to human health even at low concentrations. Their presence should thus be increasingly and extensively monitored, as their role in the overall emission context of urban and peri-urban areas is not negligible.

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