ORIGINAL RESEARCH

Experimental Application of Semi-Quantitative Methods for the Assessment of Occupational Exposure to Hazardous Chemicals in Research Laboratories

This article was published in the following Dove Press journal: Risk Management and Healthcare Policy

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Methods: We collected the data related to the chemical agents used in three different activities of three laboratories of an Italian university; the methods we compared were: MoVaRisCh, COSHH Essentials, LaboRisCh and Datarisch.

Results: The input parameters requested by each method are shown for each activity and for each used chemical. We collected the results obtained since the application of the four different tools in three tables. The use of some chemicals (especially of the activity n° three) shows a not irrelevant risk for the users.

Conclusion: Our findings show that COSHH Essentials, MoVaRisCh and Datarisch tools are consistent in the identification of a risk level; the small differences are related to risk rating, to be considered in relation with the specific structure of the method applied. The differences detected in the risk rating may be overcome by applying, for each working activity we want to assess, two or more different semi-quantitative tools. This strategy can allow to reduce the exposure to chemicals of the workers.

Keywords: chemical risk, work exposure, chemical exposure, construction industry

Introduction

The European Union's (EU) approach to risk assessment and risk management of occupational exposure to hazardous chemicals, is to resort to simplified tools compared to the quantitative surveys of the traditional Industrial Hygiene, which are based on the comparison of the environmental concentrations measured using the occupational exposure limits (OELs), in order to keep the exposure of employees within the limits prescribed to prevent work-related illness.^{1,2} The abovementioned tools are based on algorithms and will be thoroughly described in the next sections.

This approach originated primarily from the increased number of hazardous chemicals and from the shortage of resources (in terms of financial and time commitment) to carry out the sampling and analysis of airborne pollutants.^{3,4}

Moreover, owing to the high number of chemicals currently on the market, the OELs are available only for a small percentage of the hazardous substances, lower than 5%.⁵ For the chemicals without a OEL is not possible to assess a chemical

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Risk Management and Healthcare Policy 2020:13 1929–1937

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Furthermore, small and medium-sized enterprises (SMEs), which represent a significant proportion of the EU workforce,^{6,7} often experience difficulty in accessing specialist advice on occupational health and safety and they generally fail to assess the occupational exposure levels due to the high costs involved and to the difficulties in the interpretation and application of the regulation.

Finally, the chemical risk assessment is a complex activity to conduct in workplaces such as the research laboratories⁸ which are characterized by multiple microexposures, thus the performance of reliable environmental and biological monitoring may be hindered; moreover, the perception of the chemical risk diverges among the different professional profiles involved (from highly trained staff to doctoral researchers, undergraduates, and trainees).⁹

In the first half of the 1990s, new alternative approaches began to be applied (yet still complementary to the traditional methods) in the chemical risk assessment and management, based on qualitative or semi-quantitative criteria (used to evaluate and classify chemical hazards), and on the knowledge of the effectiveness of the containment technologies;^{3,10,11} in particular, various international models inspired to the Control Banding approach were developed.^{12,13} which have combined the characteristics of health hazard bands with exposure scenarios in order to establish the most appropriate control approach. Further developments of some COSHH Essentials models (for example, Stoffenmanager),14 have been applied as predictive algorithms to assess occupational exposure in the evaluation of chemical safety under the "Registration, Evaluation, Authorization and Restriction of Chemicals" (REACH) Regulation.

In Italy, following the introduction of the Legislative Decree 25/02, new algorithms have been developed, including, but not limited to, the models: MoVaRisCh,¹⁵ ArCHIMede,¹⁶ AlPiRisk (update of Inforisk),¹⁷ Cheope,¹⁸ LaboRisCh,¹⁹ the ARPA/ISPRA algorithm,²⁰ Datarisch,²⁴ which are inspired to the Control Banding (CB) logic.

Lastly, we must cite the UNI EN standard 689 (2018) which provides for the "basic characterization" of the chemical risk before proceeding with the measurement of exposure by industrial hygiene methods, taking into account the type of chemical agents, the work environment and its characteristics and the type of exposure (hazards identification, workplace inspection, identification of homogeneous groups, algorithms and any data with semi-quantitative methods).²⁵

The purpose of our study is to evaluate the application of some semi-quantitative methods. We want to identify potential bias or differences originated by applying different methods to the same activities. The aim is to verify their sensibility in indoor environment application. The working tasks are characterized by frequent changes in the operating procedures and the chemicals used (a full description of the activities is available in the next section). These characteristics of the working task can hinder a measurement of the pollutants with a quali-quantitative method.

Materials and Methods

The study was conducted in three laboratories of the Università degli Studi dell'Aquila (Italy), dedicated to water testing for the detection of Legionella spp (activity 1), to the manipulation of tumor cells (activity 2), and to the extraction and separation of cellular proteins (activity 3), respectively. The working cycle was analyzed and the following information related to the chemical substance in use was gathered:

- chemical name;
- Chemical Abstracts Service (CAS) number (CLP)
- physical state;
- volatility;
- the ingoing quantity recorded based on the scales of the relative semi-quantitative method;
- frequency and method of use;
- exposure time based on the scales of the relative semi-quantitative method;
- frequency and type of use;
- exposure times according to the scales of the semiquantitative methods.

The abovementioned informations were collected by interviewing the workers and by referring to the SDS (Safety Data Sheets) of the chemicals.

The risk assessment was performed via the algorithms MoVaRisCh, LaboRisCh, Datarisch and COSHH Essentials, whose characteristics are briefly reported below. All those algorithms are "Control-Banding based" such as many other semi-quantitative tools used in different countries.¹²

The tasks, indicated as "Activity 1", "Activity 2" and "Activity 3", have the following characteristics:

- Activity 1 has a duration which ranges from 15 to 30 minutes, it is repeated between 3 and 4 times per week and it entails the use of 4 chemical substances: mercaptoethanol, methanol, ethanol, and acetic acid;
- Activity 2 has a duration which ranges from 15 to 30 minutes, it is repeated once a week and it entails the use of 2 chemical substances: ethanol and sodium hypochlorite;
- Activity 3 has a duration which ranges from 4 to 8 hours, it is repeated between 4 and 5 times per week and it entails the use of 5 chemical substances: methanol, acetic acid, trichloromethane, hydrochloric acid, phenol.

During the activities, all the mentioned substances are used in sequence in the workflow. This is an advantage in terms of safety and risk assessment because we could change the exposure features and the PPEs (personal protective equipment) when using one or more substances involved in the work task.

Additional information about the activities can be found in the <u>Supplementary file</u>.

Methods Compared

In Table 4 we listed some useful information about the four compared methods.

COSHH Essentials Tool

The COSHH Essentials tool was selected for this study. It is the most widely used Control Banding method, developed by the Health and Safety Executive (HSE)^{21,22} and freely available via the internet.

The rationale is that even in the presence of several chemical substances and products, few distinct levels of risk (CB) result to be sufficient to control the occupational exposures to such substances.³

According to this method, the health hazard classification of a substance and a mixture of substances are based on Hazard (H) statements available from the SDS. Health hazards are grouped into five bands ranging from A (low health hazard) to E (high health hazard such as carcinogenicity, mutagenicity and respiratory sensitization) which are assigned to a logarithmic range of airborne concentration identified as providing adequate control, both for dusts and vapors.

In addiction, Hazard band S – skin and eye exposure – signifies the importance of additional control measures (Control approach S: general advice, protective gloves, personal protective equipment (PPE)) for those substances whose H-statements denote:

• irritation, corrosivity or sensitisation arising from direct contact (statements H314, H315, H317, H318, H319);

• the possibility of adverse effects resulting from absorption of substances through the skin after direct skin contact.

The determinants of exposure in COSHH Essentials^{22,23} are physical property (dustiness for solids, volatility for liquids) and amount in use. Dustiness is based on a subjective assessment that puts a substance into a high, medium or low dustiness band. Volatility is derived from the boiling point of the substance or mixture, which are allocated into a high, medium or low volatility band.

The amounts used in the task subject to assessment are divided into small (grams/millilitres), medium (kilograms/ litres), large (tonnes/cubic metres).

A third factor, duration of exposure, influences the exposure potential. This was not included in the generic risk assessment scheme. However, COSHH Essentials contain a filter for activities with a total time below 15 minutes per day.

The control approaches (CA) are grouped into four basic categories which represent the outcome of the assessment: general ventilation (CA1), engineering control (CA2), containment (CA3), special (CA4), with a progressively increasing protective efficacy.

MoVaRisCh Method

This risk assessment tool is a matrix-based algorithm, which the risk R is the result of the intrinsic hazard P of a substance or mixture multiplied with the exposure E.

For hazard P, the tool takes into account the hazardous properties for health (the H sentences provided in section 2 of the SDS related to user's health) based on the allocated score; for exposure E, the model ranks and scores type, duration of exposure, how exposure may have taken place, amount in use, effects of the preventive and protective measures.

The risk R can be calculated separately for inhalation exposures (Rinal = $P \times Einal$) and for dermal exposures (Rcute = $P \times Ecute$); in case a hazardous chemical agent may be absorbed through the skin along with the route of inhalation, the cumulative risk R (Rcum) can be obtained by calculating the square root of the sum of the squares of Rinal and Rcute.

The hazard index P and therefore the toxicological properties of a chemical agent are derived from the allocation of a value to the H-statement assigned to the most hazardous property. For the chemicals which are not considered dangerous for health, the model also allocate a P score for:

- Not dangerous chemicals that, however, contains in the mixture at least a dangerous substance;
- Not dangerous chemicals that, however, has a specified OEL.¹⁵

Therefore, a numerical hazard index is obtained (score, ranging from 1 to 10) for each chemical agent used; this methodology does not take into account the carcinogenic and mutagenic properties which are not assigned a score. The Einal inhalation exposure index is determined through the result of a Sub index I (Intensity of exposition) by a Subindex d (distance of the worker from the intensity source I):

 $Einal = I \times d$

The Sub-index I is determined on the basis of five variables, which require an accurate analysis of the technological cycle and of the work activity: physicochemical properties, amount in use, type of use, type of control, time of exposure.

Four levels are identified related to the physicochemical properties: solid state/mists (large particle size spectrum); low volatile liquids (low vapour pressure); high and medium volatile liquids (high vapour pressure) or fine dust; gaseous state.

In order to assign the corresponding level of particle size to the substances and of volatility to the liquids, the criterion identified for the COSHH Essentials algorithm is applied.

Amount in use signifies the amount of chemical agent or of the mixture actually present and to be used, by whatever method, in the working environment on a daily basis. Five different classes are identified: <0.1 Kg; 0.1-1Kg; 1-10 Kg; 10-100 Kg; >100 Kg.

With regard to the type of use, four levels, in ascending order, are identified related to the potential atmospheric dispersion: use in closed system, use in inclusion matrix, controlled and non-dispersive, use with significant dispersion.

For the type of control, the model identifies the measures that can be envisaged and implemented in order to avoid exposure to chemicals in the workplace. The hazard controls, in order of decreasing effectiveness, are: Complete containment; Ventilation – local exhaust ventilation (LEV); Segregation – separation; Dilution – ventilation. Direct manipulation.

Five intervals are identified for the daily exposure time to substance and mixture: lower than 15 minutes; between 15 minutes and two hours; between two hours and four hours; between four and six hours; more than six hours. The sub-index "d" accounts for the distance between a source of intensity "I" and the exposed worker/workers in metres: from less than to 1 metre; from 3 to 5 metres; from 5 to 10 metres; greater than or equal to 10 metres.

The output of the algorithm is a classification of the risk: irrelevant for the health (green zone), uncertainty zone (yellow), not irrelevant for health, high-risk area, serious risk area (red zone).

Datarisch Method

The assessment process through the Datarisch method includes for each chemical: filling in a risk assessment template by each worker pursuant to the classification in the CLP (Classification, Labelling and Packaging, Regulation EC No. 1272/2008) regulation reported in the Safety Data Sheets (SDS); definition of the level risk for the worker; identification of the overall risk for the worker. The Level of Risk is determined based on the following factors: intrinsic hazard P (H-statements, single or compounded, are associated in hazard classes, which are assigned a score); the amount Q of the chemical agent used (grouped into five classes: <0.1 g; between 0.1 and 5g; between 5 g and 10g; between 10g and 100g; >100g); time factor T, as a function of the activity duration (grouped into five classes: <15 minutes; between 15 and 30 minutes; between 30 minutes and 2 hours; between 4 hours and 8 hours), and the frequency of use (grouped into five classes: < once a month; between once and twice a month; once a week; between 2 and 3 times per week; between 4 and 5 times per week); the intensity of exposure factor accounts for the intrinsic characteristics (physical state and volatility), the operating temperature and for the technical and management aspects of the laboratory: number of employees present at the same time, ventilation (hourly air change rate), presence and maintenance of the collective protective equipment (CPE), management (presence and sharing) of safety information (SDS), waste management. The result identifies four potential levels of risk: not relevant risk, low relevance risk, medium relevance risk, and high relevance risk.²⁴

LaboRisCh Method

The LaboRisCh tool, which is accessible online, is structured for the assessment of health risks and defines the risk indices R_a per single agent based on the classification in the CLP regulation reported in the SDSs. The algorithm leads to the calculation of the value of a baseline risk index R_b , and therefore to a corrected risk index R_c . The value of R_c sets the relevant condition in one of three health risk bands which are identified as "green level, yellow level, red level". Moreover, LaboRisCh includes carcinogens and mutagens, whose presence entails the addition of the c/m subscript to R_c . Such addition is automatic for agents labelled as H350, H351, H340, H350i, H341 (ex statements R40, R45, R46, R49 and R68); whereas it is at the discretion of the evaluator for non «EU-classified» carcinogens that fall into the EU categories 1 or 2 and/or to IARC categories 1, 2A or 2B.

Further research has led to the integration of the algorithm: similarly to the provision for carcinogens and mutagens, the addition of the r subscript to R_c is now required for agents that are considered toxic to reproduction labelled or attributable to hazard statements H360F, H360D, H361f, H361d (ex statements R60, R61, R62 e R63). The result identifies three possible risk levels: green level, yellow level, red level.

Results

Tables 1, 2 and 3 report the levels of risk identified by the different semi-quantitative methods related to activity 1, 2 and 3, respectively. The output of the COSHH Essentials method is a control approach: in order to ensure the comparability of the results, the control approach 1 – general ventilation – was assigned to an irrelevant health hazard, whereas control approaches 2 – engineering controls, 3 – containment and 4 – special, were assigned to a greater than irrelevant risk, in increasing order of severity.

With regard to activity 1, the LaboRisCh method indicates an irrelevant risk level for all the substances. The four methods are consistent in the identification of an irrelevant risk level for ethanol.

The COSHH Essentials tool alone detects a greater than irrelevant risk for acetic acid, whereas the MoVaRisCh algorithm indicates uncertainty.

The Control Banding, MoVaRisCh and Datarisch methods identify a greater than irrelevant risk for methanol.

The COSHH Essentials and Datarisch methods indicate a greater than irrelevant risk for 2-mercaptoethanol.

It should be highlighted that the Datarisch method does not assess the hazard statement H319 for Ethanol.

With regard to activity 2, the four methods are consistent in the identification of an irrelevant risk level for ethanol whereas the MoVaRisCh method alone identifies a level of uncertainty for sodium hypochlorite.

With regard to activity 3, according to the LaboRisCh method, the risk level is not significant for acetic acid, methanol and hydrochloric acid; for phenol and trichloromethane (potentially carcinogenic and mutagenic substances) the risk level is irrelevant only if the processing is similar to that of a closed cycle. The Control Banding, MoVaRisCh and Datarisch identify a greater than irrelevant risk for all the examined substances; in particular, MoVaRisCh and Datarisch report a higher score for

Substance	Hazard	Risk Level				
Statements		COSHH Essential	MoVaRisCh	Datarisch	LaboRisCh	
2- mercaptoethanol	H301 H331 H310 H315 H318 H317 H373	2 Engineering control	R = 9.90 Irrelevant	R = 46,009 Medium relevance	R = 3.5 Irrelevant	
Methanol	H301 H311 H331 H370	2 Engineering control	R = 30.04 Greater than Irrelevant	R = 47,849 Medium relevance	R = 7.25 Irrelevant	
Acetic acid	H314	2 Engineering control	R = 19.76 Uncertainty Interval	R = 10,823 Not relevant	R = 6 Irrelevant	
Ethanol	H319	l General Ventilation	R = 9.49 Irrelevant	R = 679 Not relevant	R = 0 Irrelevant	

 Table I Results of the Semi-Quantitative Assessment Using the Four Methods of the Risk Level for 'Activity1'. The level of shading correspond to the risk level. Irrelevant risk level: none; increasing risk level: increasing shading.

Substance	Hazard	Risk Level				
	Statements	COSHH MoVaRisCh Essentials		Datarisch LaboRisC		
Sodium Hypochlorite	H314	l General Ventilation	R = 19.76 Uncertainty interval	R = 3827 Not relevant	R = 3 Irrelevant	
Ethanol	H319	l General Ventilation	R = 4.24 Irrelevant	R = 116 Not relevant	R = 0 Irrelevant	

Table 2 Results of the Semi-Quantitative Assessment Using the Four Methods of the Risk Level for "Activity2". The level of shading correspond to the risk level: Irrelevant risk level: none; increasing risk level: increasing shading.

Table 3 Results of the Semi-Quantitative Assessment Using the Four Methods of the Risk Level for "Activity 3". The level of shading correspond to the risk level: irrelevant risk level: none; increasing risk level: increasing shading

Substance	H-Statements	Risk Level				
		COSHH Essentials	MoVaRisCh	Datarisch	LaboRisCh	
Phenol	H301 H331 H311 H314 H341 H373	4 Special	R = 56.57 High	R =39,845 Medium relevance	R = 3.5 Irrelevant*	
Hydrochloric acid	H314 H318 H335	2 Engineering control	R 44.19 High	R = 32,255 Medium relevance	R = 3 Irrelevant	
Trichloromethane	H302 H315 H319 H331 H351 H361 H372	3 Containment	R = 56.57 High	R = 39,845 Medium relevance	R = 5 Irrelevant *	
Acetic acid	H314	2 Engineering control	R = 44.19 High	R = 23,432 Medium relevance	R = 6 Irrelevant	
Methanol	H301 H311 H331 H370	2 Engineering control	R = 95.47 Serious	R = 207,192 High relevance	R = 14.5 Irrelevant	

Note: *Risk may be considered irrelevant only if the processing which involves the presence of cancerogens and/or mutagens is similar to a closed cycle one.

methanol, whereas Control Banding for phenol and trichloromethane.

Limitations of the Study

Although all the illustrated semi-quantitative tools follow the CB logic, the chemical risk assessment conducted by the authors shows that the differences in the algorithms do not allow a perfect comparison between the tools. For this reason, it could be interesting to repeat the study including more

simplified assessment tools. As stated in the discussion section of the manuscript, a "basic characterization of the chemical risk" allows an assessment even before the exposure occurs. For this reason, we did not consider appropriate to compare the results with a measurement of the pollutants.

Discussion and Conclusion

In the analyzed working environment, characterized by multiple micro-exposures, a first-level assessment using

	Conceptual	Availability	Substances/	Authorship	Main Input Parameters		
	Origin		Mixtures		Health Parameters	Exposure Parameters	
COSHH Essentials	СВ	Free online	Both	HSE – UK Government	Health risk bands obtained by H Statements (or R Phrases). Band A, B, C, D,E ¹²	 Physical properties: Low, medium, high dustiness (solids); Low, medium, high volatility (boiling point of liquids (BP)); Quantity: small (g or mL); medium (kg or l); large (tonnes or m³). Duration of exposure: Number of times the worker carries out the task; duration of the task in minutes. 	
MoVaRisCh	СВ	Free online	Both	Italian local authorities (regioni Lombardia – Toscana – Emilia Romagna	Health risk scores obtained by H Statements (or R Phrases). Score from 1–10	 Physical properties: Solid state/mists; low volatile liquids (BP); high or medium volatile liquids or fine dusts; gases. Quantity: <0.1 kg; 0.1–1 kg; 1–10 kg; 10–100 kg; >100 kg; Type of use: closed system; inclusion in matrix; controlled; used with dispersion. Type of control: complete containment; local exhaust ventilation; segregation; dilution – ventilation; direct manipulation. Daily exposure time: <15 minutes; 15 min – 2 hours; 2–4 hours; 4–6 hours; >6 hours. Distance from source: <1 meter; 3–5 meters; 5–10 meters; >10 meters. 	
Datarisch	СВ	Private	Both	Infomedia (Private enterprise)	Health risk scores obtained by H Statements (or R Phrases)	 Quantity: <0,1 g; 0.1–5 g; 5–10 g; 10–100 g; >100 g. Time: <15 min; 15–30 min; 30 min – 2 hours; 4–8 hours. Frequency of use: < once per month; once – twice per month; once a week; 2–3 times per week; 4–5 times per week. Physical properties: liquid (BP); Solid; vapour; gas. Use temperature: <20°C; 20–60 °C; >60°C. 	
LaboRisCh	СВ	Free online	Both	Università politecnica delle Marche (Italian) ASUR Marche (Italian)	Health risk scores obtained by H Statements (or R Phrases). Score from 1–20	 Volatility: Solids; Low volatility liquids (BP >150°C); Medium and High volatility liquids (BP < 150°C) and fine dusts; Gases. Quantity: from 0 to 10g (or mL); from 10 to 100g (or mL); from 100g to 1kg (or l); >1kg (or l). Time of exposure: number of working days/month. 	

Table 4 Information About the 4 Semi-Quantitative Tools and Input Characteristics

an algorithm allows us to qualify the level of risk and to target the prevention and remediation efforts.

According to the purpose of the study, our findings show that COSHH Essentials, MoVaRisCh and Datarisch

tools are consistent in the identification of a risk level; the small differences are related to risk rating, to be considered in relation with the specific structure of the method applied, in particular schemes of banding/score associated with the H-statement, inclusion/exclusion of parameters related to the type of use, the current type of control approaches, and to the management and technical aspects. The differences detected in the risk rating may be overcome by applying, for each working activity we want to assess, two or more different semi-quantitative tools. This strategy can allow to reduce the exposure to chemicals of the workers by considering the assessment of the tool which assess the greatest risk level.

The LaboRisCh method detects potential risk areas only in the presence of potential carcinogens/mutagens (trichloromethane – H351 potentially carcinogenic to humans – and phenol – H341, which might induce gene mutations). For this reason it seems to be not comparable with the other three methods.

A discrepancy results from activity 1 between the two algorithms with the most similar approach, MoVaRisCh and Datarisch, with regard to 2-mercaptoethanol; since the numerical values of the indexes have not yet been published for the Datarisch algorithm, which is still in an optimisation phase, one can only assume an overestimation of the hazard statement H310 (ex R27) by the Datarisch tool.²⁴

Control Banding appears to be the most precautionary tool and it is characterized by an intrinsic operation: it allows a preliminary risk assessment in a pragmatic and precautionary approach and it enables the risk management by defining the required level of containment for each combination of substance/scenario in use, in order to ensure prevention and consistency with the existing European and Italian regulations on the occupational chemical hazards.

The MoVaRisCh algorithm, which has been validated and widely used in the Italian workplaces, allows to perform the chemical risk assessment pursuant to Article 223, paragraph 1, Title IX, of the Legislative Decree No. 81/ 2008 and subsequent amendments and additions, accounting for the parameters established by the article; it ensures the detection of deficiencies in the workstations through the "control type" (plant) and "type of use" (organizational and technological).

The Datarisch assessment method accounts for the levels of management accuracy (maintenance, training, waste management), like the LaboRisCh method; however, the extant literature does not include any validation study on the Datarisch method or the publication of the numerical values associated with the different parameters.

Acknowledgments

The study group is composed of technical and academic staff of the University of the Studies of L'Aquila: A. Civisca.

Funding

The study has been conducted by using some human and technical resources of the Università degli studi dell'Aquila. For this reason no funds have been specifically used.

Disclosure

Prof. Antonio Paoletti is now retired and is a former professor at Occupational Medicine, Università degli studi dell'Aquila, L'Aquila, Italy. The authors report no conflicts of interest in this work.

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