A PRACTICAL APPROACH TO INTEGRATED INDOOR AIR MITIGATION: GRAPH INVARIANTS CORRELATION AND SUBFLOOR-VENTILATION LAB TESTS

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Radon as an indoor air pollutant has been extensively researched worldwide over the past thirty years. However, radon is only one of several other important pollutants present in the indoor atmosphere. In addition to radon as an ubiquitous indoor pollutant, the simultaneous presence of other non-radiological pollutants, such as toxic alkanes found in the working environment, needs to be accounted for its integrated mitigation approach. Application of graph theory facilitates the study of these chemicals, using different relations (linear, logarithmic, polynomial, power and exponential) between graph invariants and the properties under study. In comparison to radon, data on exposure levels, inhalation dosimetry, and potential health effects for these non-radiological air pollutants is rather limited. This leads to a dissatisfactory situation with regard to mitigating the indoor environment: on the one hand there is the growing awareness for the need of an integrated approach to indoor mitigation, accounting for the relevant contribution of various pollutants; on the other hand, there are severe constraints in terms of manpower and financial resources, limiting the extent to which these non-radiological pollutants can be researched, when the public health policies require practically implementable advice in the near future.

In recognition of these predicaments a new pragmatic approach was taken:

a) a screening method was developed for assessing the potential of a suspected pollutant to induce health effects using graph invariants correlation analysis (GICA);
b) a simulation method was developed for conducting simplified tests on the widely used subfloor-ventilation technique under defined laboratory conditions, simulating the subsoil-pipe system with an automated soil-filled test chamber (ASTC). The ASTC is equipped with multiple sensors and externally controlled mechanical ventilation.

GICA was applied to seven alkanes found in the working environment (butane, pentane, hexane, octane, nonane, cyclohexane, trimethyl benzene). There is satisfactory correlation ($r>0.7$) between the different graph invariants and the threshold limit value-time weighted average concentration (TLV-TWA). The ASTC-experiments demonstrated the capability of this laboratory-system to allow a prediction of the performance characteristic for a given subfloor-ventilation system and certain environmental conditions.

Key words: mitigation, subfloor, invariants, regression analysis, alkanes

INTRODUCTION

A multitude of natural and man-made agents have the potential to interact with biological structures in ways leading to irreversible changes or reversible deviations from homeostasis. Because of the permanent exposure to background radiation and natural chemicals it is correct to state that any assessment of toxicity, carcinogenicity or mutagenicity of chemical, physical and biological agents should be performed as studies of combined effects [1].
Exposure to radon, especially if the activity concentrations are elevated, represents a severe problem to human health. Affected buildings need to be mitigated to reduce the health impacts on the inhabitants. Among the great variety of mitigation systems the subfloor-ventilation system is one of the most commonly used remediation methods, e.g. in Europe or USA [2,3,4]. In order to gain information on the reliability of mitigation systems and to be able to predict potential problems of such remediation systems, a test system for simulating a mitigation system under laboratory conditions was developed. This automated soil-filled test chamber (ASTC) models a soil-pipe system in combination with a fan. Air can be sucked through the soil-filled drum and a centrally located, perforated tube. The multiple sensors permit the measurement of several parameters of interest.

Certain chemicals and radiation have long been associated with mutagenic, carcinogenic effects. The diversity in chemical structure of known carcinogens and the evidence that carcinogenic effects may be mediated through different path-ways (including initiating effects, promoting effect and other mechanisms) have complicated the development of any unifying hypothesis with which to assess the carcinogenicity of all compounds [5]. It is possible to investigate chemicals for their potential to induce health effects by using the mathematical approach of graph theory. In this study chemicals found e.g. in mines, belonging to the group of toxic alkanes, were investigated. Graph theory is applied to describe the studied compounds by a scaler quantity which characterises the unknown chemical. A comparability rule [6,7] can be applied, permitting the corresponding hierarchy to be represented as the key for prediction of the unknown properties, provided the structure of the chemical under investigation is known. This involves classification of structures, i.e. their grouping into smaller units. Characterisation of structures can be accomplished by the quantification of selected structural invariants, ordering of structures which implies a decision of which among two or more structures should be taken first in a sequence [8]. With the use of nonadjacent numbers the chemical structure can be expressed by a set of numbers related to the corresponding polynomial, thereby describing the graph. Applying graph invariants correlation analysis (GICA) in this investigation linear, logarithmic, polynomial, power or exponential correlation's were studied.

The combined exposure of radon and chemicals is common indoors and in working environments, such as in mining and metallurgical industries. A special challenge is represented by the high complexity of the chemicals and their potential interactions, ranging from antagonistic, additive to synergistic effects [5].

In order to control the risk of this combined exposure it is essential to mitigate radon in a cost-effective manner and to be able to predict toxicity/carcinogenity of chemicals which act as a cofactor to radon, potentially increasing the hazard. The proposed solution combines information on the laboratory performance of mitigation systems of radon, i.e. subslab-ventilation by using the ASTC, with the application of a theoretical model GICA, which can be used as a predictive tool, for predicting the mutagenicity of xenobiotic chemicals, based on information from structure formulas only.
METHODOLOGY

ASTC

For the ASTC a 200-litre drum, with a perforated tube in its centre, was filled with soil material. Two small cylindrical containers (R1, R2) with a fine meshed bottom and lid, filled with the soil material, were placed horizontally and vertically at a filling height of 20 cm, respectively 60 cm in the drum. The soil used has been classified as "sand" [9,10] with a particle size distribution of 90.2 \% sand (2000 – 63 µm), silt 8.85 \% (63 – 2.0 µm ) and 0.95 \% clay (< 2.0 µm ). The natural radioactivity content of the soil has been analysed by gamma-spectroscopy (Bq kg^-1 dry weight): 226Ra 20.2 ± 3.5; 228Ac 13.6 ± 6.3 and 40K 165.4 ± 59.9. The drum was closed with a lid and the tube connected to a suction-fan. All seals used contained silicon. Ambient indoor air was sucked continuously through the soil material from the bottom to the top. The radon activity concentration, differential air-pressure (room air/soil gas in drum), soil gas temperature and relative humidity were measured at defined time intervals with the drum-probes. Furthermore, the loss of weight of the whole system was observed continuously. Differential pressure, temperature and relative humidity were measured by grab sampling, using the datalogger "testo 454" (testoterm). The 222Rn activity concentration of the soil gas was measured using the Lucas Cell 300A in connection with Pylon AB-5. All room air parameters were monitored with AlphaGUARD PQ2000 (Genitron).

GICA

The graph invariants correlation analysis (GICA) approach is based on the assumptions:

The geometric and electronic configuration of a molecule contains the features responsible for its physical, chemical and biological properties.

It is possible to represent a molecule by a numerical descriptor (s).

The particular advantage of graph invariants is the use of direct and simple numerical descriptors of molecular structure for quantitative correlation's with physical, chemical, biological and environmental characteristics of the molecule [11]. For the chemical characterisation in the present study three graph invariants were calculated: the nonadjacent numbers (P) [12,13], the branching index (B*I) [12,8] and the number of path length (L) [12,14]. The pollutants studied include seven alkanes found in the working environment [15]. Multiple regression analysis was applied to study the correlation's found between the calculated graph invariants and the known characteristics for the studied pollutants to predict their properties.

The following steps are required to estimate an unknown characteristic of a given chemical pollutant, provided other chemical compounds of a similar family have the same known characteristics:

1. sheet steel, 85 cm high, 60 cm diameter
2. pb-K-filtration tube DN80 (KF080N1-0.5, Hydrolit), inner diameter 80 mm, length 1.0 m, slits-width 0.5 mm
3. transparent perspex, diameter 8.4 cm, height 16 cm,
4. inline-fan (K160, Neussl), diameter 160 mm, 68 W power-consumption, 504 m³ h⁻¹ volume flow at 0 Pa pressure, 36 m³ h⁻¹ at the maximum pressure of 300 Pa.
1. identification of the chemical structure of the chemical compound under investigation.
2. graphical presentation of the chemical compound, by considering each carbon atom as a node and the bond between each two carbon atoms as an edge.
3. calculation of the graph invariants for this unknown compound.
4. repetition of step 1-3 for a similar group of compounds with the known characteristic.
5. identification of the correlation between the calculated graph invariants and the known characteristic for the studied group of compounds.
6. application of different relations (linear, logarithmic, polynomial, power and exponential) to optimise the correlation.
7. application of the comparability rule and graphical presentation of the hierarchy [4].
8. in the case of obtaining a reasonable trend, the unknown property can be predicted.

RESULTS

ASTC-System

The ASTC-system was operating from 15/5/98 to 21/11/98, whereby in the first two months the air inlet was partially blocked due to accumulation of water in the soil at the lower end of the drum. A partly heavily reduced and inconsistent air flow through the system resulted. Through an opening near the bottom of the drum a total of 860 ml water was collected in a small beaker (23/6 to 7/7). Subsequently the soil was continuously ventilated for 136 days with the fan running at full power. Due to this improper performance of the system in the first period the results up to the 7/7 were omitted for the following analysis and for the calculation of the mean values.

At the end of the investigation period the fan was stopped and the lid of the drum removed. The filling height of the soil in the drum at the end of experiment was 1.8 cm lower as compared to the start. Soil samples were taken on the soil surface and every 11 cm. For each layer three small samples (34.5 ± 2.6 g) and one large sample (215.5 ± 14.9 g) were taken. In order to determine the water loss, the soil samples were dried at 105 °C until constant weight was reached. The weight difference before and after drying was determined.

Changes of temperature and relative humidity of the room air and of the soil gas over time are shown in Figure 1 (a) and (b). The temperature of the soil gas at both measurement locations inside the ASTC followed basically the temperature of the room air, whereas for the relative humidity no correlation between the soil gas and the room air can be seen. Relative humidity of the soil gas was close to 100 % and remained constant over time. The relative humidity of the room air (daily average) showed a seasonal dependence, i.e. higher humidity in summer (June to August) as compared to the remaining months (Figure 2). In general room air temperature and atmospheric pressure were very constant over time, with mean values of 23.0 ± 1.0 °C and 967.0 ± 6.6 mbar, respectively. The mean relative humidity of the room air was 45.5 ± 13.1 %.

The average indoor \(^{222}\text{Rn}\) activity concentration was 18.1 ± 11.1 Bq m\(^{-3}\). Similar results were obtained for the analysis of the grab sample measurements of the soil gas (mean 14.4 ± 7.3 Bq m\(^{-3}\)) and of the room air (8.9 ± 5.9 Bq m\(^{-3}\)) (Figure 3).

The differential pressure in the system (drum to ambient air) remained constant over the whole period, with a mean of 2.22 ± 0.09 mbar.
Soil samples taken at the onset of the study had a mean water content between 9.8 ± 1.3 % and 10.20 % ± 1.6 %. At the completion of the study the mean water content ranged from 6.8 ± 1.0 % to 7.1 % ± 1.2 %. The water content did not show any significant local variation, independent of the sampling location inside the drum (Figure 4). The weight differences of the containers R1 and R2 before and after the experiment were 2.6 and 2.7 % and that of the reference sample R3 (container filled with the same material but exposed to room air) 10.7 %. The water content of the three samples after drying at 105 °C was 7.4, 8.1 and 0.8 %, respectively. During the investigation period the weight of the soil was reduced by 2.5 %.

GICA

The results of the theoretical approach for the toxic alkanes are shown in Tab. 1, representing the calculated graph invariants and the known characteristics of alkanes found in the working environment, potential cofactors together with radon.

The following correlation represents a case study of the practical application of multiple regression analysis in order to investigate the suitability of the correlation factor to deduce an unknown characteristic for certain compound under study. The X-axis values represent the graph invariant and the Y-axis values the characteristic of the chemical under investigation.

**A) Summation of path length versus TLV-TWA**

1. \[ Y = -30.288 x + 882.54 \] (linear \( R^2 = 0.939 \))
2. \[ Y = -472.74 \ln(x) + 1650.6 \] (logarithmic \( R^2 = 0.997 \))
3. \[ Y = 0.888 x^2 - 62.882 x + 1124.8 \] (polynomial \( R^2 = 0.995 \))
4. \[ Y = 35259 x^{-1.824} \] (power \( R^2 = 0.763 \))
5. \[ Y = 2367.8 e^{-0.133x} \] (exponential \( R^2 = 0.931 \))

**B) Branching index versus TLV-TWA**

1. \[ Y = -234.9 x + 1121.3 \] (linear \( R^2 = 0.583 \))
2. \[ Y = -754.28 \ln(x) + 1221.7 \] (logarithmic \( R^2 = 0.661 \))
3. \[ Y = 163.7 x^2 - 1277.9 x + 2680.8 \] (polynomial \( R^2 = 0.767 \))
4. \[ Y = 2476.7 x^{-2.004} \] (power \( R^2 = 0.240 \))
5. \[ Y = 1778.1 e^{-0.603x} \] (exponential \( R^2 = 0.198 \))

**C) Summation of nonadjacent numbers versus TLV-TWA**

1. \[ Y = -11.804 x + 674.28 \] (linear \( R^2 = 0.829 \))
2. \[ Y = -261.74 \ln(x) + 1129.9 \] (logarithmic \( R^2 = 0.915 \))
3. \[ Y = 0.165 x^2 - 21.952 x + 765.38 \] (polynomial \( R^2 = 0.876 \))
4. \[ Y = 4922.2 x^{-1.024} \] (power \( R^2 = 0.720 \))
5. \[ Y = 1004.2 e^{-0.0542} \] (exponential \( R^2 = 0.899 \))

The hierarchy according to the calculated nonadjacent numbers and the property TLV-TWA is shown in Figure 5. Using this approach the carcinogenity of an unknown chemical can be predicted, based only on information about its structure. This can be considered as a major step towards the prediction of the health risk of a potentially confounding agent together with radon by predicting the approximate TLV-TWA value in the ranking order within the hierarchy of similar chemicals.
DISCUSSION

The hierarchy approach can be used for the prediction of the activity of untested molecules. Figure 6 shows a descending trend from butane to trimethyl benzene for a group of toxic alkanes found in the working environment. Thus, the calculational nonadjacent numbers as a graph invariant (describing the molecule by a set of numbers) for a molecule “X” can be either positive with the same trend and therefore the predicted molecule is active, or negative and the molecule is inactive [16].

The results of the ASTC simulation experiments show that within the period of observation (136 days) this simulation represented a stable system, resulting in only small changes of the various measured ASTC system-parameters, including the differential pressure, an important quantity in radon mitigation with underpressure in the sub-slab as the main mechanism to prevent radon-entry into the building.

The loss of weight of the ASTC-system reflects the loss of water only, since no removal of soil particles has been observed. The loss of water, approximately 2 % (total system and soil samples), occurred at a constant rate resulting in a linear decrease of the total drum weight, and can be a reason for the observed constant value of the relative humidity in the soil gas. Since there were no differences observable with soil depth, this demonstrates a certain homogeneous air flow within the system. The elevated water content of the soil at the bottom of the drum is caused by gravity-induced accumulation of water. A slight increase over time has been observed for the flow rate possibly due to drying out. The initial instability of the ASTC-system is a good indicator for the significant influence of water on the performance of sub-slab ventilation systems. The soil gas temperature followed the variations of the room air, i.e. the temperature is the only parameter sensitive to ambient air conditions.

CONCLUSIONS

ASTC

The ASTC represents a mini sub-slab ventilation system, where the soil and the soil gas are the parameters under investigation, since the system can be filled with any soil material of interest. In this pilot study the soil material used was sand and it could be shown that there was no detectable effect on the soil over an investigation period of 136 days, ventilating the system with altogether 556 m³ of air at 23 °C. It can be assumed that the smaller ASTC-test system (drum) has a relatively greater sensitivity to environmental changes compared to larger systems (e.g. sub-soil ventilation beneath a building). Therefore it can be concluded that for the material tested no impacts on an installed sub-slab ventilation system should be expected, provided environmental conditions are relatively constant and that the system has been installed properly. A limiting effect on the performance of such a mitigation system therefore is primarily due to the material components, i.e. durability of the materials used, and life expectancy of fans. The importance of a proper installation of the tube-fan-system has been demonstrated in this study, particularly in view of the impeding impact of water. The ASTC-system in the laboratory can therefore assist in the identification of potential problems during the initial phase of operation of a sub-slab ventilation system.
Radon is just one indoor air pollutant, simultaneously present with other pollutants. Integrated risk assessment from exposures to mixtures of physical and chemical potentially harmful agents is a key issue in the future for all mitigation tasks. The results of this study show that it is theoretically possible to predict the carcinogenic potency of such frequently unknown chemicals in a complex environment. GICA represents an economical solution to otherwise lengthy laboratory studies of chemical pollutants with potentially toxic effects, e.g. represented by using a comparability rule and the corresponding hierarchy.

The strength of GICA remains with structural invariants being a tool for the description of a structure. Thereby the simplicity of GICA is advantageous over a curve-fitting method. Furthermore, it is applicable for the integrated risk management of the multitude of chemical substances, which are present in the working environment.

The two approaches ASTC and GICA, although completely different methodological approaches, both serve as helpful means to assist in the estimation of the effect of exposure to radon and chemicals, respectively the estimation of the performance of the radon mitigation system to be expected.

REFERENCES


Table 1: Relation between different graph invariants and the TLV-TWA$^6$ of alkanes.

<table>
<thead>
<tr>
<th>Substance</th>
<th>TLV-TWA [ppm]</th>
<th>sum of L</th>
<th>B * I</th>
<th>sum of P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Butane</td>
<td>800</td>
<td>6</td>
<td>1.9142</td>
<td>5</td>
</tr>
<tr>
<td>Pentane</td>
<td>600</td>
<td>9</td>
<td>2.4142</td>
<td>8</td>
</tr>
<tr>
<td>Hexane</td>
<td>500</td>
<td>12</td>
<td>2.9142</td>
<td>7</td>
</tr>
<tr>
<td>Octane</td>
<td>300</td>
<td>18</td>
<td>3.9142</td>
<td>34</td>
</tr>
<tr>
<td>Nonane</td>
<td>200</td>
<td>21</td>
<td>4.4242</td>
<td>35</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>300</td>
<td>17</td>
<td>3.0000</td>
<td>20</td>
</tr>
<tr>
<td>Trimethyl benzene</td>
<td>25</td>
<td>31</td>
<td>3.244</td>
<td>60</td>
</tr>
</tbody>
</table>

$^6$ Threshold Limit Value of Time Weighted Average concentration
Figure 1: Temperature (a) and relative humidity (b) of the soil gas (sampling location $T_{soil1}$ and $T_{soil2}$; $rH_{soil1}$ and $rH_{soil2}$) and of the room air ($T_{air}$, $rH_{air}$)
Figure 2: Daily average of $^{222}$Rn activity concentration, temperature, relative humidity and atmospheric pressure in the room air.
Figure 3: $^{222}$Rn activity concentration of the room air (averaged during the sampling period, AlphaGUARD) and the soil gas and room air (Pylon, grab sampling).
Figure 4: Water content of small and large soil samples before (a) and after the experiment (b).
Butane 800 ppm  
  ↓  
Pentane 600 ppm  
  ↓  
Hexane 500 ppm  
  ↓  
Cyclohexane 300 ppm  
  ↓  
Octane 300 ppm  
  ↓  
Nonane 200 ppm  
  ↓  
Trimethyl benzene 25 ppm

Figure 5: Hierarchy according to the partial sum of the calculated nonadjacent numbers and the property TLV-TWA.