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High frequency of fumigants and other toxic gases in imported freight containers – an underestimated occupational and community health risk

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ABSTRACT

Residues of pesticide fumigants and toxic industrial chemicals in freight containers represent a health hazard to employees and consumers, especially since freight containers are sealed for transport and distributed widely throughout the importing countries before being opened for unloading.

We investigated 2113 freight containers arriving at the second largest container terminal in Europe, Hamburg, Germany, over a 10-week period in 2006. The countries of origin, type of contents and the pesticide fumigation history declared on labels attached to the container were recorded.

We determined that 1478 (70%) containers were contaminated with toxic chemicals above chronic reference exposure levels (RELs), 761 (36%) even exceeded the higher acute REL thresholds. Benzene and/or formaldehyde contamination was 4-times greater than for fumigants.

Our findings indicate a health risk for dockworkers, container unloaders and even end-consumers, especially as many of the cancerogenic or toxic gases elude subjective detection.

benzene, bromomethane, hydrogen phosphide, pesticides
Competing Interest: None to declare
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INTRODUCTION

The advent of the use of freight containers and globalisation, with the recent export of manufacturing production from industrialized societies to the new economies and the subsequent reimport of the finished goods, has resulted in a substantial increase in international trade. The vast majority of internationally transported goods is shipped in freight containers and this represents a trade volume that has increased six-fold, within the last two decades, to over 400 million containers annually.\textsuperscript{1,2} The fumigation of transported goods with toxic chemicals was introduced to protect plants or plant products and human or animal foodstuffs from infestation and destruction by pests, according to the phytosanitary requirements stipulated by either the importing country or the International Plant Protection Convention (IPPC). The increasing incidence of freight container fumigation has been exacerbated by a 2002 edict, ISPM No.15\textsuperscript{3} by the Food and Agriculture Organization (FAO) of the United Nations, which requires either bromomethane fumigation or heat treatment and appropriate labelling of the wood used for packaging, palettes and container floors. At sufficiently high concentrations, all fumigants are toxic\textsuperscript{4} and since many fumigants (notably the cancerogenic halogenated hydrocarbons bromomethane and 1,2-dichloroethane) are colourless and have high subjective odour thresholds then dangerous exposure may occur unwittingly. Our original objective was to determine the art and extent of residual fumigant contamination in import containers for an assessment of possible health risks. Our observations revealed a greater and much more widespread problem of container air contamination by toxic industrial chemicals, especially formaldehyde and benzene, with numerous known deleterious effects on the body, from acute airway irritation to cancer and immediate death.\textsuperscript{3,4}
METHODS

2113 import freight container air samples were analyzed during a 10-week period in 2006 (from 25 July to 30 September) in order to assess the incidence of gaseous contaminants. The set of 2113 investigated freight containers consisted of every fourth container from the 8029 selected for random detailed X-ray surveillance by the Customs Authority, Waltershof, Port of Hamburg, from the 540,000 import containers arriving at the port of Hamburg, Germany, during these 10 weeks. Countries of origin, classification of goods and incidence of fumigant warnings were recorded.

Air samples from the containers were obtained using stainless steel penetration probes that were pushed through the rubber seals of the container doors to a depth of 30 cm. These aspirated samples, after discarding the dead volume, were collected in three minutes into two new 1 L Tedlar bags within a Vac-U-Case (Analyt-MTC GmbH & Co. KG, Müllheim, Germany). The principle limitation of a study in the field is the absence of a single measuring device that is selective and sensitive to all fumigants and volatile toxic compounds and, so, mobile laboratory analyses were performed using two different mass spectrometry methods. The selected-ion flow-tube mass spectrometer (SIFT-MS, Voice 100; Syft Technologies Ltd, Christchurch, New Zealand) quantifies chemicals by detecting specifically selected ions5 and it is programmed for the detection of compounds based on prior experience and preliminary findings. The limits of detection of target compounds using SIFT-MS were 10 ppb of bromomethane, 100 ppb ethylene oxide, 250 ppb hydrogen cyanide, 5 ppb hydrogen phosphide, 100 ppb sulphuryl difluoride and 5 ppb of formaldehyde.

The transportable gas-chromatograph mass spectrometer (GC/MS EM 640, Bruker Daltoniks GmbH, Bremen, Germany) uses a temperature programmable gas chromatograph coupled to a mass spectrometer to measure retention time (small gas chromatograph column) and mass spectra to identify unequivocally volatile organic compounds in complex mixtures6,7. The EM 640 features direct GC/MS coupled with a ruggedized one-piece quadrupole filter and electron multiplier to provide the mass spectra. The signal intensity of selected mass peaks can be used for quantitation of pre-selected target compounds and characteristic fragmentation patterns, produced by the sample ionization, can be used to deduce the molecular structure of an unknown compound. Samples were measured after aspiration and limits of detection down to 10 ppb 1,2-dichloroethane, 30 ppb trichloronitromethane and 3 ppb benzene were achieved.

The SIFT-MS instrument can be operated with minimal training and can also measure molecules that are either undetected (i.e. inorganic fumigants such as hydrogen phosphine, hydrogen cyanide) or poorly resolved (i.e. highly volatile substances with less affinity for the column, such as bromomethane, sulphuryl difluoride) by the portable EM 640. In contrast, the resolving possibilities of EM 640 and its ability to make an unbiased identification, without preselection of candidate chemicals, requires highly trained and qualified personnel for its successful operation.

Mass spectrometry data was evaluated in relation to the Reference Exposure Levels (RELs) released by the Office of Environmental Health Hazard Assessment (OEHHA)8. These RELs are designated chronic RELs because they based on the most sensitive relevant health effect reported in the medical and toxicological literature for a particular target tissue and are designed to protect the individuals who live or work in the vicinity of emissions of these substances. Chronic RELs are determined as concentrations or doses at, or below which, adverse noncancer health effects are unlikely to occur in the general human population, assuming that a population threshold exists below which adverse effects do not occur.
In contrast, the higher thresholds of the acute RELs are time-weighted average values from the OEHHA and reflect the requirements for health and safety during occupational exposure. Where no acute RELs were available, equivalent levels were obtained from the recommended exposure limits of the National Institute for Occupational Safety and Health (NIOSH). The NIOSH recommended exposure limits are considered to be independent science-based recommendations rather than legally applicable standards.

People who are unaware that a chemical has been applied in a particular area will be unable to take the relevant precautions and, therefore, have to be treated like the general public with the provision of an adequate margin of safety in such a situation. Unlike ships, unopened fumigated freight containers are distributed deep within the importing country and unloaded mostly by unschooled or unwitting workers.

Evaluation of the data was performed using descriptive statistics with univariate analysis. Subgroups were formed according to three major categories, namely country or region of origin, the type of goods or contents as declared to the customs authorities and the type of contaminating chemical detected during the course of the investigation, which were further subdivided into seven representative subsets for data analysis and ease of graphical representation.
RESULTS

External inspection of the 2113 containers revealed that none of the containers had valid Dangerous Goods Transport Documentation as stipulated for fumigated units in chapter 5.4.2 of the IMDG Code.\textsuperscript{11} Only 3.6\% of the 2113 containers carried any form of fumigation hazard warning at all, although none corresponded to the fumigation warnings required by the IMDG Code and mostly consisted of fragments of old, presumably outdated, warning signs, some in oriental script, from previous freight shipments.

Consistent with the globalisation of modern trade,\textsuperscript{12} 1202 of the 2113 investigated import containers were of Chinese origin (56.9\%), with 264 (12.5\%) from SE Asia and 120 (5.7\%) from the Indian Subcontinent (Fig. 1A). Of the remaining four geographical regions (South America, Europe/North America, Middle East and Africa), each contributed only about 5\% to the imported container sample, with 138 (6.4\%) arriving from the rest of the world, either from areas outside of these defined regions or where the country of origin was unknown.

Analysis of air samples from these 2113 containers determined that 1478 containers (70\%) contained at least one of seven major fumigants and/or toxic industrial chemicals above chronic RELs (or limit of detection when >REL). When ranked according to frequency of contamination, nearly three quarters of the containers imported from China (74.5\%) exceeded these levels for the investigated and identified chemicals (Fig. 1B). The next most contaminated containers were from Middle East (71.4\%), followed by South America (69.0\%), Europe/North America (65.2\%), the Indian Subcontinent (63.3\%) and SE Asia (62.9\%) whereas containers from Africa were not only low in number (70/2113; 3.3\%) but more often free of contaminating chemicals (rank 7; 51.4\% >chronic RELs). Thus, the proportion of contamination above chronic REL (reflected in the rankings 1 to 7) and the absolute numbers of containers exported from a particular region (as indicated by the spectral colours in Fig. 1A) are in general agreement. This is also the case for the incidence of contamination above the acute REL thresholds, with only Europe/North America showing a distinct improvement at these higher, generally occupational, cut-off levels.

The major categories of imported goods (Fig. 1C) were clothes/textiles (28.4\%), furniture/household (18.1\%) and manufactured goods (16\%), followed by natural products (10.6\%), foodstuffs (9.6\%), electrical appliances (8.4\%) and, lastly, shoes (7.5\%), with only 29 (1.4\%) containers unclassified according to these categories. When assessed according to type of goods, 87.3\% of the containers containing shoes exceeded chronic RELs, followed by furniture/household (78.5\%), foodstuffs (75.4\%) and electrical appliances (71.2\%) (Fig. 1D). Manufactured goods (67.0\% >chronic RELs) were unduly influenced by the inclusion of only 17 containers loaded with tools that were highly likely to be contaminated (88\%), while natural products (63.6\%) were less contaminated. The least contaminated clothes/textiles category (61.8\%) nevertheless represents a rather frequent exposure as nearly every fourth container arriving at the port belongs to this latter category (600 from 2113).

The data in Fig. 1D demonstrates more of an inverse relationship between the ranking of the likelihood of contamination and the absolute numbers of imported types of goods (as indicated by the order of spectral colours in Fig. 1C). Clothes/textiles are the most imported product category and yet least likely to be contaminated (red, rank 7) and shoes containers are few in number but with a high likelihood of contamination (violet, rank 1). The notable exception to this trend is the furniture/household category, ranked second in both number of imported containers and likelihood of contamination. Interestingly, the electrical appliances category performed better than the other categories at the higher acute REL thresholds.
The seven major fumigant or toxic industrial chemicals that were detected at concentrations above chronic RELs (limit of detection) on 2201 individual occasions in the air samples from 1478 contaminated containers (with multiple contamination occurring in 493 containers) are ranked in Fig. 2 according to their frequency of contamination. For comparative purposes, the likelihood of contamination by a particular chemical has been normalised to 100% for each category of country or goods. The most frequent contaminants were formaldehyde (1252) and benzene (408), with the remaining containers exhibiting residual fumigant contamination, notably from bromomethane (294) and hydrogen phosphide (95), followed by 1,2-dichloroethane (90), trichloronitromethane (35) and ethylene oxide (27). The frequencies of other fumigants were mainly low (n = 3, 0.15 % sulphuryl difluoride, suggested as a substitute for the ozone-depleting bromomethane) or not found (hydrogen cyanide).

Containers from China were the most likely to be contaminated and this is essentially independent of the category of goods, as was also observed but to a less marked degree for the Indian Subcontinent and SE Asia (Fig 2A). As mentioned formaldehyde was the major contaminant for all countries of origin and, to a lesser degree, benzene, bromomethane and hydrogen phosphide. Trichloronitromethane and ethylene oxide contamination at low frequencies was a characteristic of containers mainly from SE Asia, the Middle East and the Indian Subcontinent. Analysis of contamination according to shipped goods revealed that the contents categories of furniture/household, foodstuffs and natural products were consistently more likely to be contaminated, regardless of the countries of origin (Fig. 2B). Formaldehyde was again the most likely contaminant at high frequency and in all categories, but especially in foodstuffs and furniture/household items. Benzene contamination was also widespread but was most prevalent in shoes and less common in foodstuffs and clothes/textiles. Of the classic fumigants, all but the textiles/clothes category had incidences of bromomethane of 15-24%, while hydrogen phosphide was quite a frequent contaminant of foodstuffs and found to a lesser extent in the other goods categories. The other fumigants were only infrequent contaminants of mainly furniture/household items, foodstuffs, and natural products, except for a higher incidence of 1,2-dichloroethane in shoe containers further exacerbated by the high co-contamination with benzene.

Figs 2C and 2D reveal the incidence of contamination above the higher, occupationally defined, acute RELs. Even at these higher thresholds of the acute RELs, 761 (51%) of the 1478 contaminated containers originally defined by the chronic RELs were still contaminated, of which 111 were multiply contaminated by at least two toxic chemicals at these higher thresholds. Generally, the pattern of contamination by a particular chemical was similar for the acute and chronic cut-off thresholds, except for some variation in the chronic and acute REL transgressions for formaldehyde and bromomethane among the different geographical regions. Normalised incidence frequencies are useful for the comparison, but may mask absolute extent of the toxic contamination, so that the 2774 incidences of chemical contaminations for the five fumigants and two solvents were compared in relation to the individual chronic and acute RELs (Fig. 3). For each individual substance at least single containers showed contaminations manifold exceeding the acute REL limits. On one occasion, the level of hydrogen phosphide was 120,000 times the acute REL. The concentrations exceeding Immediately Dangerous to Life or Health (IDLH) were found in 0.6% of the contaminated containers.
DISCUSSION

Container air samples from a random representative selection of 2113 containers, arriving at the port of Hamburg, were measured in a mobile laboratory for evidence of chemical contamination using two complementary mass spectrometry methods [with a broad analytical spectrum]. The aim of the study was to identify chemicals being used as fumigants and to collect preliminary data about the extent of possible residual contamination with these substances. This is the first report in this field indicating that the air in a large number of imported containers may present health risks not only from fumigant residues but also from toxic industrial chemicals.

Although there are some reservations about the universality of our study (the restricted range of analysed chemical, their limits of detection and possible seasonal or regional issues), the incidence of contamination above chronic and/or acute reference exposure levels appears widespread, regardless of type of contents or countries of origin of the containers. The contamination of certain goods from particular countries was more likely and deserves some attention. Shoes were particularly problematic, most often contaminated at high levels (87.3% above chronic RELs) and generally sourced from China or SE Asia, with a few from the Indian Subcontinent. A greater cause for concern is that the next most likely contaminated contents were furniture and household items, followed by foodstuffs, providing ample opportunities for chemical contamination, both at home and in the workplace as well as from ingestion. Shipments of tools (as a component of manufactured goods) were often and highly contaminated by toxic industrial chemicals (88.2%), although their absolute numbers were mercifully low (0.8% of 2113 containers). Although clothes/textiles had the lowest frequency of contamination (61.8% above chronic and 24.7% above acute RELs), they were the most frequently shipped goods and found in every fourth container (28.4%), making their overall contribution and likelihood of exposure high. The limits of detection for several contaminants (bromomethane, hydrogen phosphide, ethylene oxide, hydrogen cyanide and formaldehyde) were equal to or above the defined chronic RELs and, therefore, their actual incidence of contamination could be underestimated by the mobile laboratory analyses.

Among the fumigants, exposure to bromomethane concentrations must be of primary importance, with 13.9% of import containers with contaminant levels above chronic and 1.1% above the acute RELs. The most likely category of goods to be contaminated with bromomethane was shoes at 24.1% >chronic REL (0.0% >acute REL), predominantly in import containers from South America and Middle East. Hydrogen phosphide is the most frequently used fumigant in the world and it was most often found in foodstuffs at 14.8% (5.4% >acute REL), whereas 1,2-dichloroethane (mostly detected in containers from China, especially in those with shoes) seems to play a hitherto unknown role in either fumigation, disinfection, insecticide or production processes.

Container air was not only tainted with different fumigants but also contaminated with various toxic industrial chemicals to a much greater extent, with formaldehyde and benzene concentrations above chronic (and acute) RELs in 59.3% (30.9 %) and 19.3% (5.0 %) of containers, respectively. It is not known if these industrial chemicals originate from the phytosanitary process itself or are associated with the manufacturing or packaging processes. Formaldehyde toxicity is experienced after inhalation of vapours and causes bronchial irritation, pneumonia and pulmonary edema at high concentrations.14,15,16,17 Formaldehyde may also increase the risk for nasopharyngeal squamous cell carcinoma and contribute to UV-induced skin carcinogenesis.18,19

The high incidence of benzene contamination, especially in shoe containers from China (at 29.6%; as opposed to a 21.3% incidence for all other types of goods from
China), suggests that this carcinogenic chemical banned in most Western countries is still broadly used elsewhere. Benzene is known to have toxic effects on the blood, bone marrow and cerebrum at high concentrations, but it has also been shown to lower leukocyte and platelet counts even at levels far below the acute REL of 410 ppb. The carcinogens bromomethane, 1,2-dichloroethane and benzene may also have cumulative effects at low concentrations.

Fumigants and other toxic industrial chemicals are not only present in the container atmosphere but also in transported goods (manuscript in preparation). The unintentional exposure to such toxic chemicals has been reported to be associated with accidents and diseases, some with fatal outcome, e.g. due to neurological or respiratory ailments, including Reactive Airways Dysfunction Syndrome (RADS) and pulmonary edema, endangering dockworkers, seafarers, employees of port authorities and import companies, as well as other workers handling the fumigated goods and even end-consumers. A more detailed survey of exposed subjects is urgently needed. Only then will the full extent of the health risks from inhalative exposure to these chemicals be determined.
Fig. 1:  
A) Major countries of origin for the 2113 sampled import containers.
B) The 1478 containers chemically contaminated above chronic reference exposure levels (>chronic RELs, coloured bars) are ranked according to frequency of contamination but coloured according to country of origin from fig 1A. The higher acute RELs are indicated by a vertical bar and encompass 761 more highly contaminated containers.
C) Major types of goods for the 2113 sampled import containers.
D) The 1478 containers chemically contaminated above chronic reference exposure levels (>chronic RELs, coloured bars) are ranked according to frequency of contamination but coloured according to type of goods from fig 1C. The higher acute RELs are indicated by a vertical bar and encompass 761 more highly contaminated containers.

The chronic and acute reference exposure levels in ppb were from the Office of Environmental Health Hazard Assessment (OEHHA) for the following industrial solvents and fumigants where available, otherwise they were from the National Institute for Occupational Safety and Health (NIOSH, italics): formaldehyde 2.44, 76; benzene 18, 410; bromomethane 1.28, 1000; hydrogen phosphide 0.6, 300; 1,2-dichloroethane 98, 1000; trichloronitromethane 0.06, 100; ethylene oxide 16.6, 100; sulphuryl difluoride 5.13, 5000; hydrogen cyanide 8.2, 300.

Fig. 2: Normalised frequencies of the detected fumigants and toxic industrial chemicals above chronic RELs (A and B) in 1478 contaminated containers and above acute RELs (C and D) in 761 contaminated containers for country of origin (A and C) or type of goods (B and D), ranked according to incidence of contamination in Figs 1B and 1D, respectively.
Grey quadrants indicate zero containers with a particular constellation of chemical and country of origin or type of goods.

Fig. 3: Distribution of the 2774 incidences of chemical contamination (in ppm) in the 1684 contaminated containers, in relation to limits of detection (LOD, black), chronic as well as acute RELs as given in the legend to Figure 1. The data points for the incidences of contamination accumulate from the highest measured level to the lowest.
Concentration is plotted on a log scale for convenience; the area under the curve is thereby meaningless and only the position and trend of the curve is interpretable,
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This manuscript is the first research in this field showing that import containers not only remain contaminated with residues of the applied fumigants but also exhibit a more frequent and greater contamination by the toxic industrial chemicals formaldehyde and benzene. 70% of container air samples were contaminated with at least one of seven major fumigants and industrial solvents at concentrations above chronic reference exposure levels, with 36% even exceeding the higher acute reference exposure levels. 0.6% had concentrations Immediately Dangerous to Life or Health and, on one occasion, the level of hydrogen phosphide was 120,000 times the statutory limit. The application of fumigants and toxic industrial chemicals is known to cause accidents and disease, some with fatal outcome. These findings are related to global and local public health. The information is relevant to many medical and other disciplines as well as to public health policy in order to raise awareness of the possible toxic exposure problems and health risks.
A Country of origin

B Incidence of contamination by country of origin

C Type of goods

D Incidence of contamination by type of goods