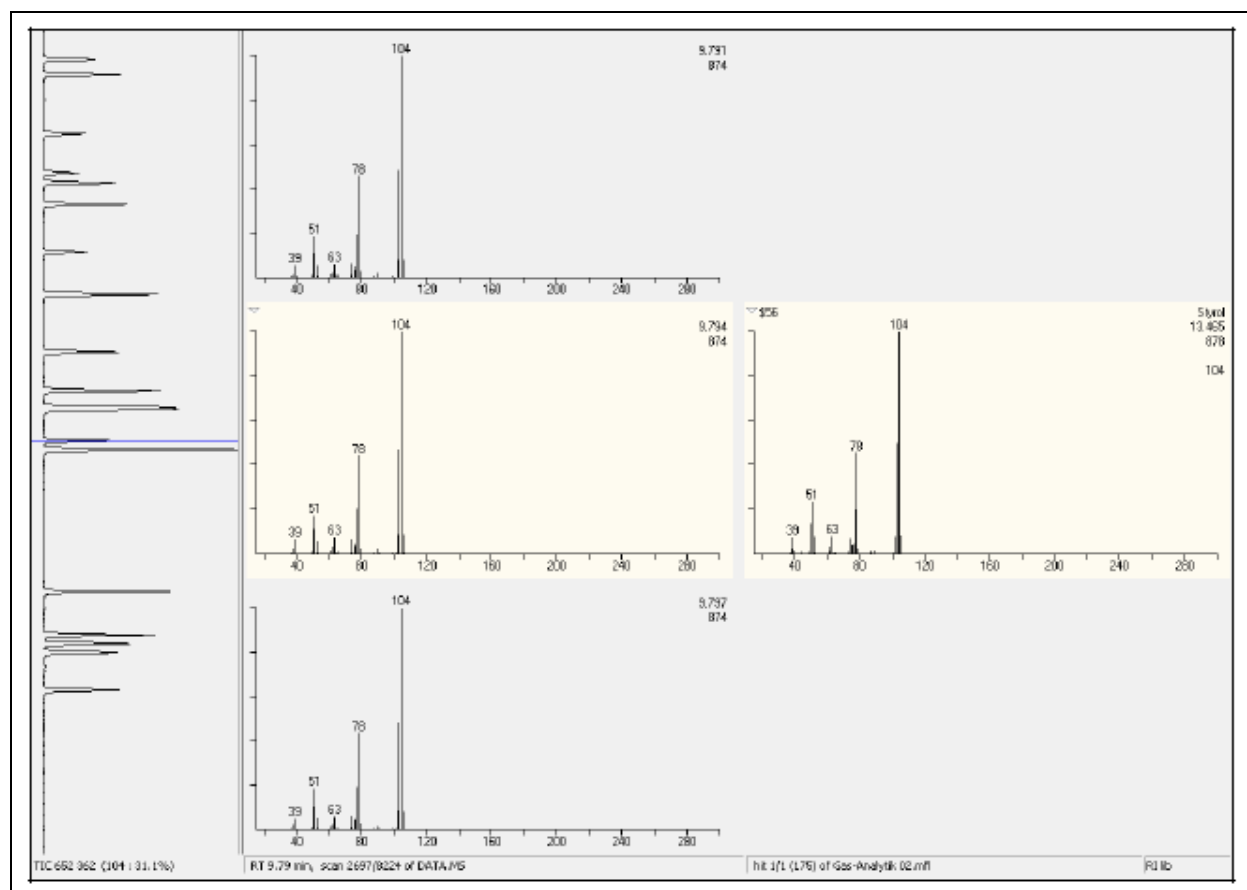
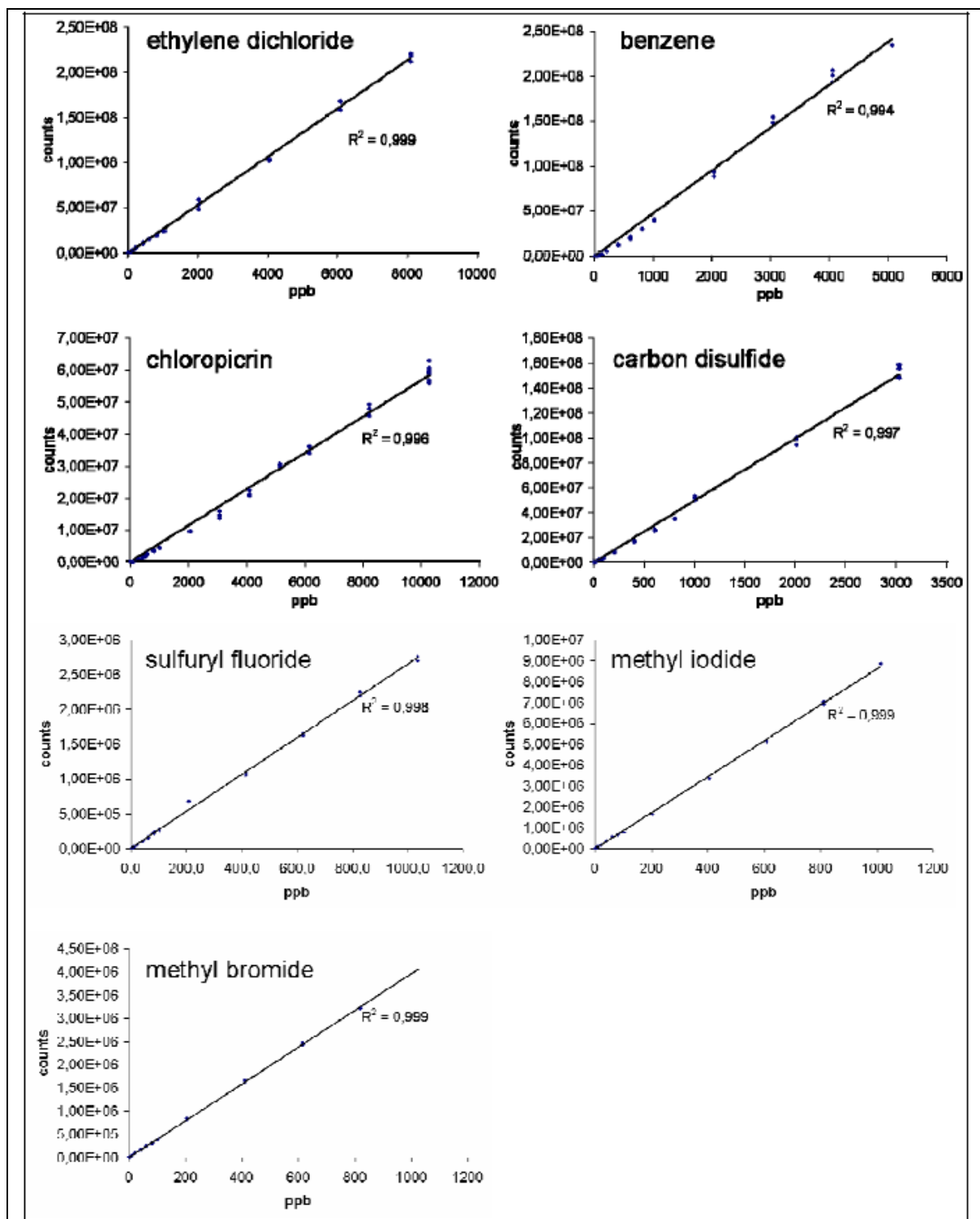


## Halogenated Hydrocarbon Pesticides and some other Volatile Organic Contaminants and their Residues Provide Analytical Challenges in Global Trading

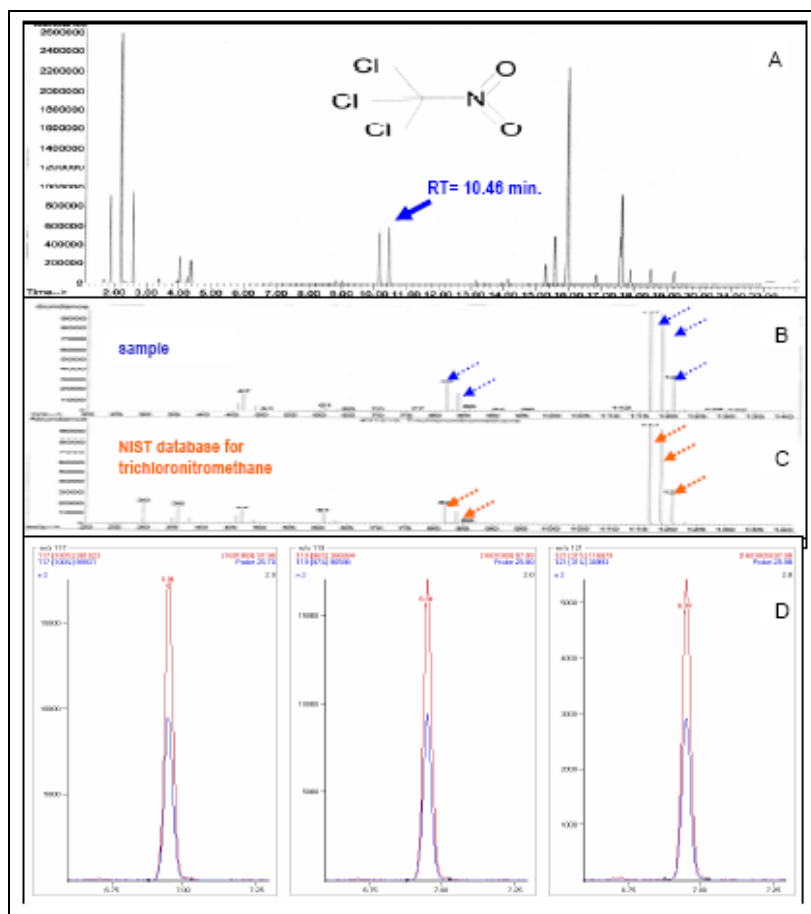
Lygia T. Budnik, Svea Fahrenholtz, Stefan Kloth and Xaver Baur



**Supplementary figure 1: Analysis of a container air sample for non-target analytes by applying “Mass Finder” Software to the mass spectrometric scan data (see Experimental).**



Supplementary figure 2: Examples of standard curves for different target analytes in TD-GC/MS Analysis



**Supplementary figure 3: Identification and quantification of chloropicrin (trichloronitromethane) in a complex mixture of volatile hydrocarbons:**

**A** Chromatogram in TIC mode shows the separation of peaks and the chloropicrin peak at 10.46 min. **B/C**: MSD ChemStation screenshot: **B** Mass spectrum of chloropicrin recorded during sample analysis. **C** Mass spectrum of chloropicrin in NIST database. **D** Multi trace analysis allowing quantification of chloropicrin and to show the consistency of the MSD spectra (in each chosen m/z) between the analyzed sample (blue) and the chloropicrin standard (red).

Chemical Substance (Synonym or trade name)	Acute effects	Possible carcinogenic effects	Chronic effects		
Halogenated hydrocarbon fumigants	Occupational exposure limit (OEL) (in ppb)	Potential Carcinogen = + (Class)	Community exposure levels (CEL) (in ppb)	Limit of Detection (LOD) (in ppb)	Conversion
	TWA (8h)				
1,3-dichlorpropene (DCP; 1,3-dichloro-1-propene)	1,000 b	+ b	7 f	5	1 ppb = 4.54 µg/m <sup>3</sup>
ethylene dichloride (1,2-dichloroethane; EDC, DCE)	1,000 b	+ (2) b,d	98 e	0.5	1 ppb = 4.05 µg/m <sup>3</sup>
methyl bromide (bromomethane)	1,000 a	+ (3) b,d	50 f	1	1 ppb = 3.89 µg/m <sup>3</sup>
methyl iodide (iodomethane)	2,000 b	+ b		0.5	1 ppb = 5.80 µg/m <sup>3</sup>
methyl chloride (chloromethane)	50,000 b	+ (3) b,d	50 f	1	1 ppb = 2.07 µg/m <sup>3</sup>
methylene chloride (dichloromethane)	25,000 b	+ (3) b,d	115 e	1	1 ppb = 3.47 µg/m <sup>3</sup>
propylene dichloride (1,2 dichloropropane)	75,000 b	+ b	50 f	1	1 ppb = 4.62 µg/m <sup>3</sup>
terachloromethane (carbon tetrachloride)	500 c	+ (3) b,d	30 e		1 ppb = 6.29 µg/m <sup>3</sup>
<b>Other fumigants, volatile pesticides</b>					
carbon disulfide (carbon bissulfide)	1,000 b	-	275 e	0.5	1 ppb = 3.11 µg/m <sup>3</sup>
chloropicrin (trichloronitromethane nitrochloroform)	100 b,c	-	0.06* e	2	1 ppb = 6.72 µg/m <sup>3</sup>
sulphuryl fluoride (sulfuryl difluoride)	5,000 b	-	5 e	1	1 ppb = 4.18 µg/m <sup>3</sup>
<b>Other volatile industrial solvents</b>					
benzene (benzol, phenyl hydride)	1,000 c	+ (1) b,d	18 e	0.5	1 ppb = 3.19 µg/m <sup>3</sup>
ethyl benzene (phenyl ethane)	100,000 c	+ b	460 e	2	1 ppb = 4.34 µg/m <sup>3</sup>
toluene (methyl benzol, toluol, phenyl methane)	50,000 c	-	80 e	0.5	1 ppb = 3.77 µg/m <sup>3</sup>

(a) •OEHA (Office of Environmental Health Hazard Assessment). Air Toxics: acute and chronic reference exposure levels for airborne toxic [http://www.oeaha.ca.gov/air/acute\\_rels/acuterel.html](http://www.oeaha.ca.gov/air/acute_rels/acuterel.html)

(b)•NIOSH (The National Institute for Occupational Safety and Health: recommended exposure limits <http://www.cdc.gov/niosh>

c•European Union, Scientific Committee for Occupational Exposure Limits to chemical Agents (SCOEL), <http://osha.europa.eu/publications>

d• IRAC (International Agency for Research on Cancer, WHO, <http://www.iarc.fr>)

e•OEHA (Office of Environmental Health Hazard Assessment). Air Toxics: chronic reference exposure levels for airborne toxicants

[http://www.oeaha.ca.gov/air/chronic\\_rels/acuterel.html](http://www.oeaha.ca.gov/air/chronic_rels/acuterel.html)

f• ATSDR: Agency for Toxic Substances and Diseases Registry. Minimal Risk Levels (MRLs) for Hazardous Substances

<http://www.atsdr.cdc.gov/mrls.html>. US Department of Health and Human Services; \*• CEL below LOD

**Supplementary table 1: Health-based exposure reference values for methyl- and ethyl halide based pesticides and other contaminants.**

<b>NAME [CAS Number]</b> <b>(Synonyms)</b>	<b>target toxicity</b>	<b>R</b>	<b>N</b>	<b>S</b>	<b>R/D</b>	<b>T</b>
<b>halogenated hydrocarbon fumigants</b>						
<b>1,3-dichlorpropene</b> [ 542-75-6 ] (DCP; 1,3-dichloro-1-propene)		X	X	X		X
<b>ethylene dichloride</b> [52399-93-6] (1,2-Dichloroethane; EDC, DCE)		X	X	X		X
<b>methyl bromide</b> [ 74-83-9 ] (bromomethane)		X	X	X	X	X
<b>methyl iodide</b> [74-88-4] (Iodomethane)		X	X			X
<b>methyl chloride</b> [ 74-87-3 ] (chloromethane)			X	X	X	
<b>methylene chloride</b> [75-09-2] (dichloromethane)		X	X	X		X
<b>propylene dichloride</b> [ 78-87-5 ] (1,2 dichloropropane)		X	X	X	X	X
<b>terachloromethane</b> (carbon tetrachloride)				X		
<b>other fumigants, volatile pesticides</b>						
<b>carbon disulphide</b> [75-15- ] (carbon bissulfide)			X	X	X	X
<b>chloropicrin</b> [ 76-06-2 ] (trichloronitromethane nitrochloroform)		X				X
<b>sulphuryl fluoride</b> [2699-79-8] (sulphuryl difluoride)		X	X	X		X
<b>other volatile industrial solvents</b>						
<b>benzene</b> [71-43-2] (Benzol)		X	X	X	X	X
<b>ethyl benzene</b> [ 100-41-4 ] (ethylbenzol, phenylethane)		X	X			X
<b>toluene</b> [ 108-88-3 ] (methyl benzene, toluol)		X	X	X	X	X

References: Centers for Disease Control and Prevention, NIOSH Pocket Guide to Chemical Hazards (<http://www.cdc.gov>) and United States National Library of Medicine, National Institutes of Health, Haz-Map (<http://hazmap.nlm.nih.gov>)

**Supplementary table 2: Likely affected target organs after intoxication with air contaminants identified in the study. (Respiratory (R), Neurotoxic (N), Systemic (S), Reproductive/developmental (R/D), Topical (T))**

Unit	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
contaminants (in ppb)																				
ethylene dichloride	530,000	<0.5	3,241	5,522	<0.5	<0.5	<0.5	<0.5	<0.5	973,000	5,522	104,532	3,242	86,445	512,000	857,000	75,801	<0.5	8,251	8,000
methyl bromide	<1	5,800	<1	<1	7,787	7,082	<1	<1	840,000	<1	<1	<1	<1	<1	<1	<1	<1	7,707	2,000	2,013
methylene chloride	70,000	<1	901,000	4,711	<1	<1	<1	10,000	1,000	<1	4,711	86,000	902,000	58,000	11,960	902,000	58,000	<1	24,000	<1
propylene dichloride	<1	<1	239,000	532,000	<1	<1	<1	<1	<1	<1	360,000	<1	<1	<1	<1	238,000	<1	<1	<1	<1
tetrachloro- methane	1,910	<1	7,000	<1	<1	<1	20,000	<1	<1	<1	<1	<1	<1	<1	1,900	<1	<1	<1	<1	<1
carbon disulfide	<0.5	<0.5	<0.5	1,651	<0.5	<0.5	44,000	<0.5	<0.5	976,000	1,651	<0.5	532,000	<0.5	9,000	975,000	<0.5	<0.5	<0.5	<0.5
chloropicrin	<2	200,000	<2	<2	13,000	37,000	<2	<2	25,000	<2	<2	<2	<2	<2	<2	<2	54,000	13,000	<2	<2
benzene	363,000	0.8	5,001	9,343	0.5	7,000	12,000	4,560	<0.5	40,000	9,345	2,947	<0.5	<0.5	257,000	<0.5	1,501	<0.5	1,329	4,559
toluene	2,006	5,000	18,261	9,529	3,000	34,000	122,428	27,673	27,000	12,314	9,529	1,217	<0.5	31,915	5,564	<0.5	736,000	3,000	150,000	709,800

**Supplementary table 3: Multiple air contaminations in individual containers:**

The single representative data from 20 individual import containers (regularly arriving in Rotterdam and Hamburg 2006-2008) is chosen to pint point how the analyzed container air samples vary from one analyzed unit to the other. The samples were quantified by TD-GC/MS.