

Hazard identification and risk assessment for a former industrial chemical plant

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The site

- Production plant producing chemical intermediates for the pharmaceutical and chemical industry including aroma essences, biocides, preservatives, binders etc.
- Operation 1960 - 1997



Production units

- Benzyl cyanide unit
- Phenyl acetate unit (yellow hall)
- Dithio salicylic acid unit
- Benzal phthalide unit (blue hall)
- Technical unit (pilot plant)
- Storage of failed production batches (waste)

Events leading to shut down

- Disagreements with the authorities
- Non-adherence with discharge permits
- Accumulation of chemical waste
- Bankruptcy
- The responsible company abandoned the site

Site investigations

- 1993 – 2005
- Extensive soil and groundwater pollution
- Extensive soil air pollution
- Remedial groundwater project
- Removal of chemical waste

Situation 2005



Production Plant close to private dwellings



The problem

- Uncertainty about human health risks for private housing close to the site
- Medical Officer required a representative study
- Concerns about whether previous studies had been sufficiently comprehensive
- No complete list of chemicals used at the site had been prepared or evaluated

Objectives for this study

- Identify a “complete” list of chemicals and potential degradation products
- Collect data on physical chemical properties
- Identify potential transport and exposure routes for different chemical groups
- Collect data on toxicological properties and quality criteria
- Identify critical chemical entities (acute toxic at low conc., long term effects, carcinogenic/mutagenic)
- Identify analytical techniques to screen or quantify the critical entities
- Assess consequences due to **uncertainty**

Method

- Make a chronological historical list of information from environment permits, authority inspections and investigation reports etc. in the “**Historical data**” sheet in a spreadsheet
- For each report/permit, list the chemical entities cited and note the media in which they were found or the production protocol
- Identify each new entity with a chemical identity number
- Enter each new chemical entity in the “**Chemical data**” sheet in the spreadsheet

Historical sheet

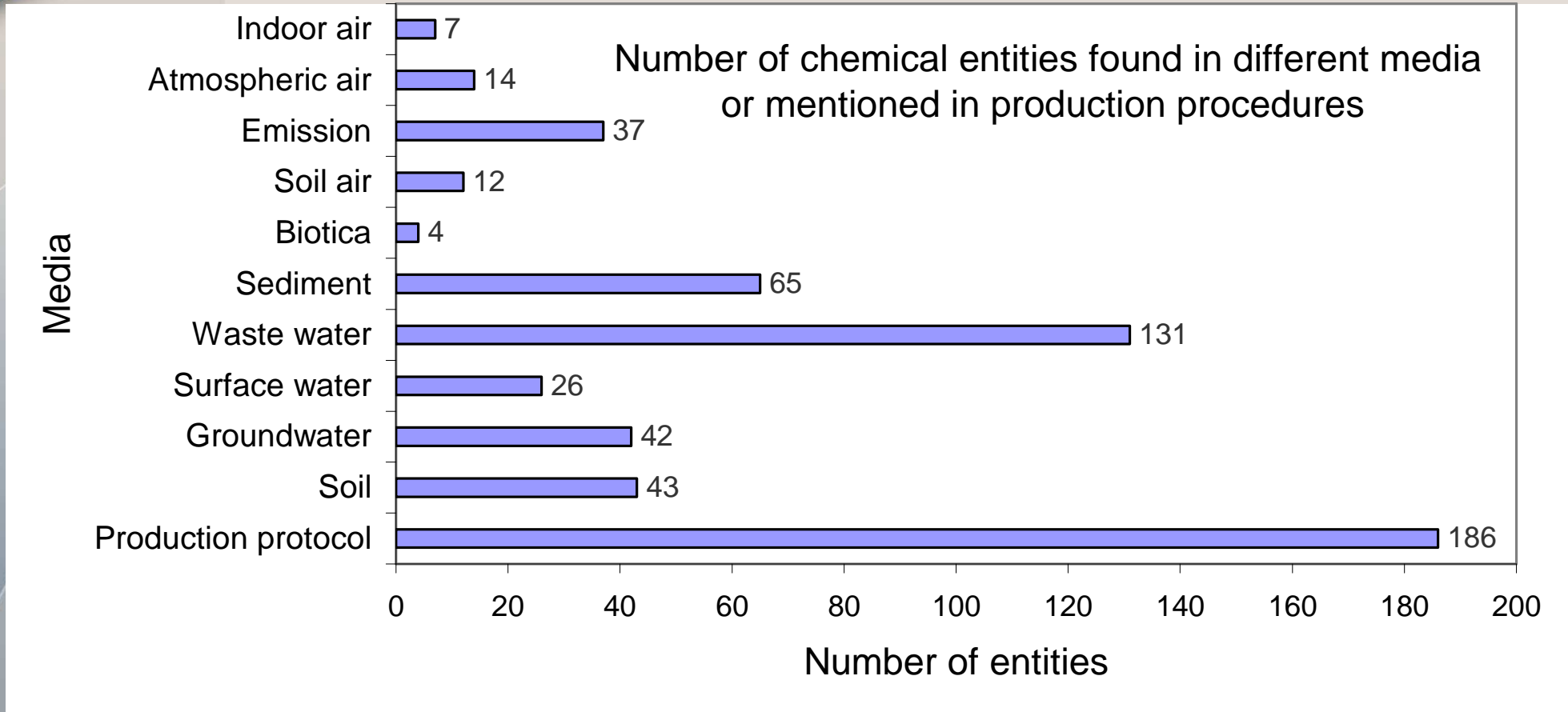
Year	Historical event	Chemical entity	Entity I.D.	Production protocol	soil	Ground water	Surface water	Waste water	sediment	Biotica	Soil air	Emission	Atmospheric air	Indoor air	Reference
1960	Chemical Factory moved to locality	Tetrachloromethane	152	P											Environmental permit 1992.
1974	Analysis of waste water	<u>Tetrachloromethane</u>	152					W							Report 1974
1974	Analysis of waste water	Tetrachlorethylen	4					W							Report 1974

Chemical data sheet

Chemical group	Chemical entity	Chemical I.D.
Chlorinated aliphatics		
	1,1,1-trichlorethan	151
	1,1-dichlorethylen	233
	1,2-cis-dichlorethylen	235
	1,2-trans-dichlorethylen	234
	Tetrachlorethylen	4
	Tetrachlormethan	152



Overview of chemical entities



370 chemical entities identified
after careful weeding out of synonyms!

Classification in 25 chemical groups

- Hydrocarbons
- Chlorinated aliphatics
- Chlorinated aromatics
- Aliphatic alcohols
- Aromatic alcohols
- Phenols and chlorophenols
- Mercaptans, thiols and sulphides
- NSO-heterocycles
- Organic acids
- Aldehydes
- Ketones
- Amines
- Anilines
- Ethers
- Alkyl Cyanides
- Nitriles
- Alkyl chlorides
- Anhydrides
- Organic salts and esters
- Phthalates
- Amides
- Cyanides
- Inorganic chloride/bromide/chlorite compounds
- inorganic salts
- Production Residues

Chemical data sheet

Chemical group	chemical entity	Chem. I.D.	CAS-nr.	Synonym	mol. wt.	Boiling point	Vapour Pressure (20-25°C)	Solubility (20-25°C)	Log K _{ow}	pKa	Henrys Constant	References
					g.mol	°C	Pa	mg/l			Pa.m ³ .	
Aliphatic alcohols												
	1-heptanol	403	111-70-6	n-heptyl alcohol	116,2	176	29	1670	2,41		1,9E+00	2, 4
	1-hexanol	404	111-27-3	n-hexyl alcohol, amylcarbinol	102,2	158	123	5900	2,03		1,7E+00	2, 4
	1-octanol	405	111-87-5	1-octyl alcohol, caprylic alcohol	130,2	195	10,6	540	2,8		2,5E+00	2, 4
	2-butoxyethanol	2	111-76-2	Butylcellosolve, butylglycol	118,2	168,4	117	1000000	0,83	-	1,6E-01	2, 4, 5
	Ethanol	144	64-17-5	Ethylalkohol	46,1	78,2	8000	1000000	-0,31	16	5,1E-01	4, 5
	Methanol	193	67-56-1	Methylalkohol, træsprit	32	64,6	12265	1000000	-0,82	15	4,6E-01	2, 4, 5
	Nonanol	402	143-08-8		144,3	213	3,02	140	3,1		3,8E+00	2, 4

Only 220 (60 %) identified by a CAS-no.

Only 170 (46%) assigned physical chemical properties

Chemical data sheet

chemical group	chemical entity	Chemical I.D.	Analytical technique		Labelling			Classification (based on pure entity without dilution)
			Air	Water	Danger symbols	Risk labels	Safety labels	
Aliphatic alcohols								
	1-heptanol	403	CS-rør	P&T				
	1-hexanol	404	CS-rør	P&T	Xn		22 (2)-24/25	Xn;R22
	1-octanol	405	CS-rør	P&T				
	2-butoxyethanol	2	CS-rør	P&T	Xn	20/21/22-36/38	(2)-36/37-46	Xn;R20/21/22 Xi; R36/38
	Ethanol	144	CS-rør	P&T	F		11 (2)-7-16	F;R11
	Methanol	193	CS-rør	P&T	F, T	11-23/24/25-39/23/24/25	(1/2)-7-16-36/37-45	F;R11 T;R23/24/25-39/23/24/25
	Nonanol	402	CS-rør	P&T				

A sample collection medium (i.e. for air samples) and an analytical technique was identified where possible.

Results

- List of chemical entities expected in soil air (or indoor/outdoor air)

Carbon dioxide	Cyanide	N-methylbenzylamine
1,1,1-trichloroethane	Diethyl aniline	Nitrogen dioxide
1,1-dichloroethylene	Diethyl carbonate	Nonanal
1,2-CIS-DICHLOROETHYLENE	Diethyl disulfide	O-CHLOROTOLUENE
1,2-TRANS-DICHLOROETHYLENE	Diethyl oxalate	Octanal
1-heptanol	Diethyl phthalate	<u>o-fluorbenzylchloride</u>
1-hexanol	Dimethylcyanamide	O-XYLENE
1-octanol	Acetic acid anhydride	<u>Parafluorbenzylchloride</u>
2,6-dimethylaniline	Ethanol	<u>p-chlorbenzylchloride</u>
2-butoxyethanol	ETHYLBENZENE	P-CHLOROTOLUENE
2-chloraniline	<u>Ethyl bromide</u>	Phenol
Acetonitrile	<u>Ethyl methylbenzene</u>	<u>Phenylacetylchloride</u>
Ammoniac	Formaldehyde	Piperazine
Ammoniac water	Hydrogen	P-XYLENE
Aniline	<u>Heptane</u>	STYRENE
BENZALDEHYDE	Hexane	<u>Sulfurylchloride</u>
BENZENE	<u>Hexanal</u>	Sulphur dioxide
BENZOIC ACID ETHYLESTER	<u>Hexanacid</u>	TETRACHLOROETHYLENE
<u>Benzonitrile</u>	Hydrogen cyanide	<u>Tetrachloromethane</u>
BENZYLALKOHOL	Hydrogensulfide	<u>Thionylchloride</u>
<u>Benzyl amine</u>	Isopropyl benzene	TOLUENE
<u>Benzylchlorid</u>	<u>m-chlorotoluene</u>	<u>Trichloromethane</u>
<u>Benzyl cyanide</u>	Methanol	<u>Trichlorobenzene</u>
<u>Benzyl dimethylamine</u>	Methylamine	TRICHLOROETHYLENE
BENZYLETHYLETHER	<u>Methylethylketone</u>	VINYL CHLORIDE
Hydrogen peroxide	METHYL-ISO-BUTYL-KETONE	<u>α-methylstyrene</u>
Carbon disulfide	<u>Methylphenylacetate</u>	
<u>Chlorbenzene</u>	M-XYLENE	
Hydrogen chloride	Formic acid	
	<u>N,N-dimethylbenzylamine</u>	

- List of chemical entities expected in groundwater

Results - testing of analytical procedures

	Chemical i.d.	PL1 - Blue hall	PL2 - Yellow hall
		$\mu\text{g}/\text{m}^3$	
Benzene	6	-	4,4
Toluene	10	5,3	11
Ethylbenzene	156	3,4	1,7
Xylens	74	5,3	5,6
C ₉ -C ₁₀ aromates		3,6	3,4
Acetone		11	18
Dichloromethane		20*	30*
Trichloroethylene	3	-	4,1
Tetrachloroethylene	4	3,7	16
Other compounds at concentrations less than $5\mu\text{g}/\text{m}^3$		28	21
Total volatile oragnics (TVOC)		82	110
Formic acid (CS-tube)	348	21	12
Acetic acid (CS-tube)		40	83

Air sampling using a combination of ATD-tenax and ATD-chromsorb 106 with GC/MS-screening

Results - testing of analytical procedures

	Quality criteria	403 Feb. 2000	505 Maj 2006	505 Aug. 2006	507 Maj 2006	507 Aug. 2006	Blind Aug. 2006
$\mu\text{g}/\text{m}^3$							
Chlorinated solvents							
Tetrachloroethylene	6	140	-	-	10	-	-
Trichloroethylene	1	-	-	-	-	-	-
Trichloromethane	20	-	-	-	-	-	-
Tetrachloromethane	5	-	-	-	-	-	-
1,1,1-trichloroethane	500	-	-	-	-	-	-
1,1-dichloroethylene	10	-	-	-	-	-	-
1,2-cis-dichloroethylene		-	-	-	-	-	-
1,2-trans-dichloroethylene	400	-	-	-	-	-	-
Aromatics							
Benzene	0,13	50	-	-	-	-	-
Toluene	400	1.300	-	33	19	33	22
m/p-o-xylene	100	380	-	-	-	13	-
C ₉ aromates			-	-	-	-	-
C ₁₀ aromatics	30		-	-	-	-	-
p-cymene			11	-	-	-	-
Aliphatic Hydrocarbons							
n-Decane			-	-	-	-	-
n-undecane			-	-	-	-	-
C ₁₃ -C ₁₅ alkane			-	-	-	-	96
C ₇ -C ₁₆ alkanes			-	-	-	-	-
Cyclohexane	(1000)		-	-	-	-	-
2,2-dimethylhexane			-	-	-	-	-
Ethylcyclohexane			-	-	-	-	-
Prom chemicals							
Benzothiazole			-	42	-	14	63
Acetone	(400)		66	-	-	-	-
Chlorobenzene	(100)		-	-	-	-	-
Chlorotoluene		-	-	-	-	-	-
1,2-dichloro-3-methylbenzene			-	-	-	-	-
Chloromethylbenzene			-	-	-	-	-
1-Chloro-2-methylbenzene			-	-	-	-	-

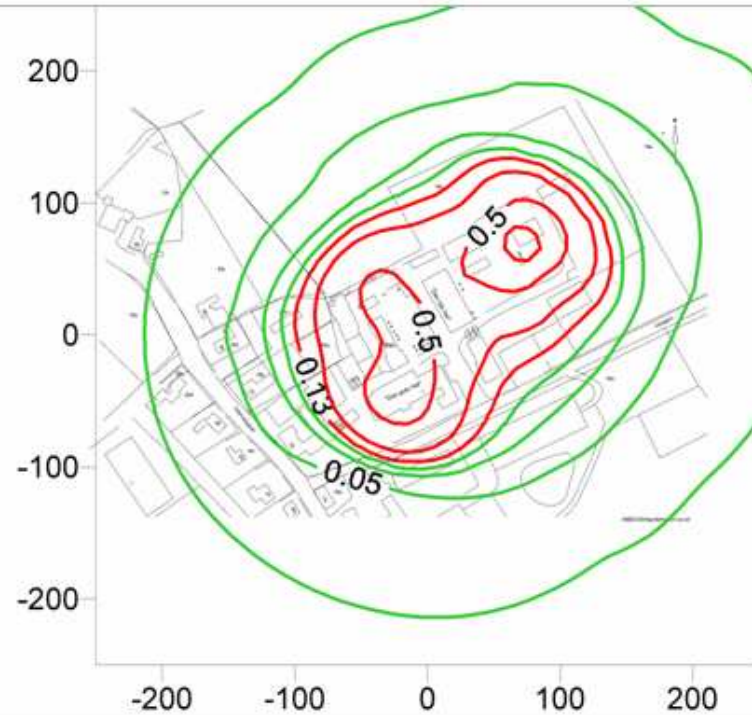
Results - testing of analytical procedures

	Quality criteria	403 Feb 2000	505 Maj 2006	505 Aug. 2006	507 Maj 2006	507 Aug. 2006	Blind Aug. 2006
µg/m ³							
Aroma essences							
Alpha-pinene	(50)		3.300	6.800	-	-	
Beta-pinene			88	360	-	-	
Camphene			180	490	-	-	
Limonene	100		98	180	-	-	
beta-Myrcene			35	91	-	-	
b-Phellandrene			-	-	-	-	
D-verbenone			34	-	-	-	
3-carene			-	-	-	-	
Germacrene B			-	-	-	-	
3-thujen-2-ole			18	-	-	-	
e-7-11-dimethyl-3-3-methylen-1,6,10-dodecatriene			-	-	-	-	
Other chemicals							
Acetic acid	(100)		120	-	40	-	
Formic acid	(3)		-	-			
1,3-dichloro-2-methylpropane			-	-			
2-ethyl-1-hexanole			-	21		12	
3-octanone			-	-			
6,6-dimethyl-2-methylen-bicyclo[2,2,1]heptan-3-one			15	-			
Unidentified			13	25			
Unidentified-CS			-	20			
Sum of other TVOC			110	240	<50	180	<50
TVOC	100		3.900	8.300	<50	250	180

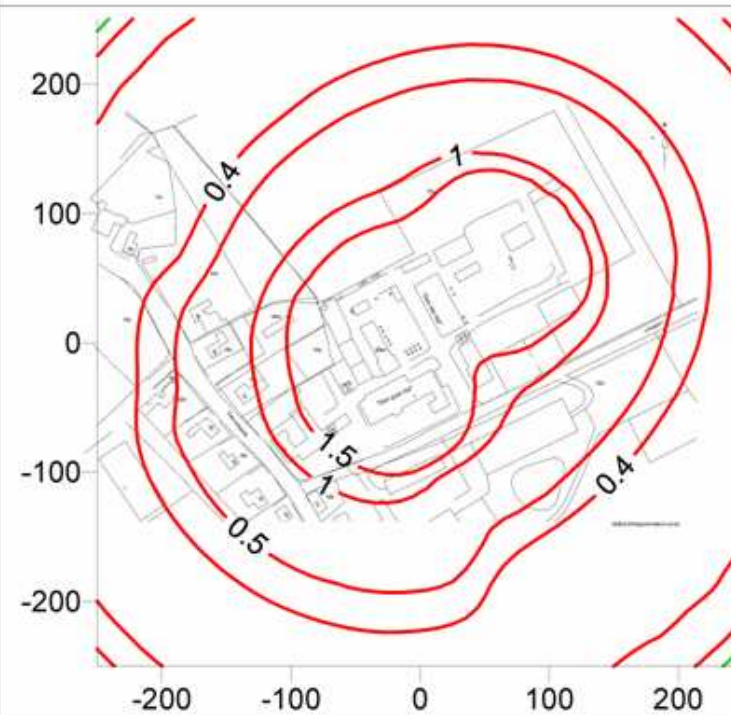
Air sampling using a combination of ADT-tenax and ADT-chromsorb 106 with GC/MS-screening

Modeling of atmospheric spreading

Scenario 1 – benzene:
Mean yearly value ($\mu\text{g}/\text{m}^3$)



Scenario 1 – benzene:
Maximum for the monthly 99% fractile ($\mu\text{g}/\text{m}^3$)



Conclusions

- Study identified a list of chemicals of concern
- Special analytical screening techniques for groundwater and air samples were developed and tested
- Major contaminants already identified by the previous investigation were in fact the critical contaminants with respect to the risk assessment
- Sensitivity calculations of atmospheric spreading showed that relatively high flux from the soil surface produced only minimal effects outside the perimeter of the installation, which was in agreement with actual measurements

Conclusions

- Study identified a number of compounds which could be used as indicators for spreading of pollution from the site to the private dwellings
- A program for a representative investigation was devised and approved by the Medical Officer