Electronic Supplementary Material (ESI) for Journal of Environmental Monitoring

Exposure assessment methodology for Tetrafluoroethylene (TFE) and Ammonium perfluorooctanoate acid (APFO)

Introduction

Semi-quantitative exposure assessment was carried out for each occupational title at each plant for discrete periods of time throughout the history of plant operation. Each plant was visited by at least one occupational hygienist to collect all relevant information including information on production processes, general ventilation, local ventilation etc. Details of process changes such as the introduction of automatic or semi-automatic systems, local ventilation etc were recorded.

Interviews were carried out with key plant personnel both to obtain a description of the historical development of the plant and to acquire descriptions of each of the occupations identified at the initial stage. This includes descriptions of the tasks performed and frequency (how long each shift and how often per year). Information was also collected on control measures, including local ventilation and personal protective equipment. Finally, details of changes in tasks and working practices throughout the period of operation of each plant were also collected.

The semi-quantitative exposure assessment method used in this study was based on that developed and used by Semple (2004) in the GeoParkinson study to assess both cumulative and average annual intensity of exposure to various chemicals on an individual basis. These metrics were calculated using the job description and information on frequency (both how long exposure lasted during each shift and how often subjects were exposed each year). Exposure was classified into broad groups: high, medium and low. Using a combination of estimated exposure intensity, the exposure frequency (number of days per year), a frequency adjustment to take account of the number of hours per day of exposure and the exposure duration (number of years of contact) both cumulative exposure and average annual intensity metrics were calculated.

Since the purpose of this project was to assess exposure for each job, only exposure intensity, exposure frequency and frequency adjustment are of interest.

Intensity of exposure

Exposure to TFE and APFO was considered in each area by considering exposure in different areas over the entire production period. The first plant started production in 1951. Starting production dates for the other plants range from 1952 to 1979. Over the entire study period, 1951 to 2002, the highest exposures would have occurred in the polymerisation area during the early 1950s. Due to the introduction of control measures, increasing process automation and other improvements over the years in all plants, exposures will have decreased and are likely to be well below the exposure limit (8.2 $mg.m^{-3}$ or 2 ppm for TFE and 10 $\mu g.m^{-3}$ for APFO), with most being low or very low.

An exposure matrix was generated for both TFE and APFO for each area of the plant as it would have been in the early 1950s. Inhalation exposure was of interest for TFE and inhalation, dermal and ingestion exposures for APFO.

Table 1 – Exposure matrix for each area of the plant

Area	TFE	APFO
Monomer		
Cracking	Medium	-
Distillation	Low	-
Autoclaves/polymerisation	High	High
Finishing		
Dispersion grades	Very low	Low
Other grades	Very low	-
Control room [1]	-	-
Gallery	Low	Low
Maintenance	Medium	Medium
Research & development	Very low	Very low

1 if control room is separate from the other areas

The starting exposure categories are defined in table 2.

Table 2 – Exposure categories

Category	Median
High	1000
Medium	300
Low	100
Very low	30

Exposure intensity was then modified according to any other factors which might affect exposure, e.g. ventilation, protective equipment, workplace. Guidance on appropriate modifying factors has been provided by Cherrie (1999) and Cherrie *et al.* (1996). Details of guidance on these modifiers was adapted and reproduced from Semple (2002) below.

For a particular job, exposure intensity was selected based on the area of the plant the operator was working in at the start of the production period. For plants where production started much later, e.g. 1979, the starting exposure intensity was much lower.

Over time in all plants there were improvements in technology and cleanliness and to account for this each decade exposure intensity was reduced by 10%. The starting exposure levels for each decade are shown in table 3.

Table 3 – Starting exposure levels for each decade

Decade	High	Medium	Low	Very low
1950s	1 000	300	100	30
1960s	900	270	90	27
1970s	810	243	81	24
1980s	729	219	73	22
1990s	656	197	66	20

Modifiers guidance

***Ventilation*:** if effective ventilation (LEV) was described exposure was decreased by a factor of 3. If very effective LEV was described the value was decreased by a factor of 10.

PPE: if frequent use of PPE is reported then the multipliers in table 4 were used.

Table 4 – PPE multipliers

Type of PPE	Multiplier
Inhalation exposure	
RPE (frequent use):	
Full-face positive pressure respirator	0.025
Other	0.25
Dermal exposure	
Gloves	0.92
Overalls	0.38
Rubber boots	0.90
Gloves + overalls	0.30
Gloves + rubber boots	0.82
Overalls + rubber boots	0.27
All three	0.19

An explanation of how the dermal exposure figures were calculated is given in appendix 1.

Confined space: if the subject reported working in small confined spaces such as a tank or a small sealed room then exposure was increased by a factor of 3.

Outside work: this reduced exposure by a factor of 3.

Form of APFO used: when it was used in powder form, between 0.5 and 8 kg was weighed, which could result in high exposure levels. Change to the automatic liquid dispensing system decreased exposure by a factor of 3. This change resulted in handling and emission changes

Supervisors: they usually only had background exposure. Exposure was reduced by a factor of 10. However, when they assisted the operator directly then exposure was reduced by a factor of 3.

Cleanliness: an increase in cleanliness was accompanied by a 10% decrease in exposure.

Leaks: In the early days there were more problems with leaks and over time there were gradual improvements in technology which reduced exposure. If there is no information, exposure was reduced by 10% for each decade.

Exposure frequency

Information on exposure duration was provided in the job descriptions. For workers working 8 hour shifts it was assumed that an average worker worked for 5 days per week for 44 weeks per year (220 days). In most plants 12 hour shifts were usually worked, although some operators worked day shift. Overall all operators worked the same number of hours per year as those working day shift. Those working 12 hour shifts worked 147 days/year. Frequency values are listed for those working 8 and 12 hours shifts in Table 5 and 6, respectively.

Table 5 - Default values for frequency of exposure (8 hour shifts)

Description	Frequency value
Every day	220
2-3 times per week, regularly	110
Once per week, occasionally	44
Once per month, rarely	12
Once per year, very rarely *	1

* note some tasks were only carried out once/year but were carried out over a period of several days

Table 6 - Default values for frequency of exposure (12 hour shifts)

Description	Frequency value
Every day	147
1-2 times per week, regularly	74
Once per week, occasionally	25
Once per month, rarely	7
Once per year, very rarely *	1

* note some tasks were only carried out once/year but were carried out over a period of several days

Frequency units were adjusted depending on the number of hours per day that the worker was in contact with the substance. This information was obtained from the job descriptions which included the amount of time an operator spends on each task. The frequency adjustment was expressed relative to an eight-hour working day (Table 7). For example, two hours per day resulted in the frequency units being adjusted by a factor of 0.25.

Table 7 – Frequency adjustment

Number of contact hours per day	Frequency adjustment
0.5	0.063
1	0.125
2	0.25
3	0.375
4	0.5
5	0.625
6	0.75
7	0.875
8	1
9	1.125
10	1.25
11	1.375
12	1.5

Calculation of exposure

There was no dermal exposure to TFE and so the adjusted exposure intensity for a particular task was then calculated as follows:

Adjusted exposure intensity = [base exposure intensity x exposure modifications]
x exposure frequency (days/year)/220 x frequency adjustment

Since there was both inhalation and dermal exposure to APFO, the adjusted exposure intensity for a particular job was calculated as follows:

Ajusted exposure intensity = [base exposure intensity x exposure modifications]
x [(proportion inhaled x rpe) + (proportion dermal x ppe)]
x exposure frequency (days/year)/220 x frequency adjustment

The assessor decided what proportion of exposure was due to inhalation and what proportion could be ascribed to dermal exposure.

This gave a numeric value for exposure.

A particular job was split up into tasks and the above equation applied to calculate exposure for each task. Exposure for each task was summed to obtain the total exposure for that job.

The equation was separated into three sets of adjustments for:

1. Cleanliness and leaks
2. Ventilation, RPE, PPE, confined work, outside work and for supervisor
3. Frequency of contact and the number of hours of contact/year

Cleanliness and Leaks

$$AI_1 = BEI - (BEI \times Cleanliness) - (BEI \times Leaks)$$

Ventilation, RPE, PPE, confined work, outside work and for supervisor

$$AI_2 = \frac{AI_1 \times RPE \times Confined\ \ space}{Ventilation \times Outside \times Supervisor}$$

or for APFO exposure

$$AI_2 = \frac{AI_1 \times Confined\ \ space}{Ventilation \times Outside \times Supervisor \times APFO\ form}$$

$$\times \left[(Inhalation\ \ proportion \times RPE\ multiplier) + (Dermal\ proportion \times PPE\ \ multiplier) \right]$$

Frequency of contact and the number of hours of contact/year

$$E = AI_2 \times \frac{Frequency\ of\ contact}{220} \times \frac{No.\ of\ hours\ contact\ /\ day}{8}$$

This was the annual exposure for a particular job.

where *BEI* – Base Exposure Index

AI_i – ith Adjusted Index

E – Estimated exposure

The default for cleanliness and leaks is 0.

The default for RPE, PPE, confined space, ventilation, outside worker and supervisor is 1.

The starting point for the next time period is AI_1.

Example – polymerisation operator – TFE exposure

This is a fictional simplified example and does not represent a polymerisation operator from any particular plant in the study. The dates are also fictitious.

The polymerisation operator was exposed to TFE only during cleaning. Cleaning was carried out on a daily basis. From 1975 to 1980 the operator worked eight hour shifts. This was a daily task (frequency of exposure is 220 days) which was carried out for approximately 1.5 hours (frequency adjustment is 0.1875). There were three time periods for consideration:

1975 – 1980	
1981 – 1990	Reductions in leaks
1991 – 2000	Improved extract system, reduction in leaks

From table 1, the BEI was defined as being high. As the starting period was in the 1970s, the exposure level is 810 (from table 2).

1975 – 1980

$$AI_1 = 810 + 810$$

Note, there were no adjustments for cleanliness or leaks since this was the first time period

$$AI_2 = \frac{810 \times 1 \times 1}{1 \times 1 \times 1} = 810$$

$$E = 810 \times \frac{220}{220} \times 0.1875 = 152$$

1981 – 1990

$$AI_1 = 810 - (810 \times 0.1) = 729$$

$$AI_2 = \frac{729 \times 1 \times 1}{1 \times 1 \times 1} = 729$$

$$E = 729 \times \frac{220}{220} \times 0.1875 = 137$$

1991 – 2000

$$AI_1 = 729 - (729 \times 0.1) = 656$$

$$AI_2 = \frac{656 \times 1 \times 1}{3 \times 1 \times 1} = 219$$

$$E = 219 \times \frac{220}{220} \times 0.1875 = 41$$

Example – polymerisation operator – APFO exposure

This is a fictional simplified example and does not represent a polymerisation operator from any particular plant in the study. The dates are also fictitious.

The polymerisation operator was exposed to APFO when cleaning and when weighing APFO powder. Both tasks were carried out on a daily basis. Cleaning was a daily task (frequency of exposure is 220 days) initially carried out for approximately 1.5 hours (frequency adjustment is 0.1875). He spent 15 minutes three times/shift weighing APFO (frequency adjustment is 0.09375). From 1975 to 1980 the operator worked eight hour shifts, working 12 hour shifts from 1981 onwards. There were three time periods for consideration:

1975 – 1980	Overalls were worn at all times. In addition, gloves and a dust mask were worn when weighing APFO.
1981 – 1990	APFO was now weighed in a weighing booth with extract ventilation. There were reductions in leaks. PPE was as above.
1991 – 2000	Automatic APFO liquid dispensing system introduced. PPE was as above. There were reductions in leaks

From table 1, the BEI was defined as being high. As the starting period was in the 1970s, the exposure level was 810 (from table 2).

1970 – 1980

$$AI_1 = 810 + 810$$

Note, there were no adjustments for cleanliness or leaks since this was the first time period

$$AI_2 = \frac{810 \times 1}{1 \times 1 \times 1 \times 1} \times \left[(0.7 \times 0.25) + (0.3 \times 0.3) \right] + \frac{810 \times 1}{1 \times 1 \times 1 \times 3} \times \left[(0.3 \times 1) + (0.7 \times 0.3) \right] = 215 + 138$$

$$E = 215 \times \frac{220}{220} \times 0.09375 + 138 \times \frac{220}{220} \times 0.1875 = 20 + 26 = 46$$

1981 – 1989

$$AI_1 = 810 - (810 \times 0.1) + 810 - (810 \times 0.1) = 729 + 729$$

$$AI_2 = \frac{729 \times 1}{3 \times 1 \times 1} \times [(0.7 \times 0.25) + (0.3 \times 0.3)] \times \frac{729 \times 1}{1 \times 1 \times 1 \times 3} [(0.3 \times 1) + (0.7 \times 0.3)] = 64 + 124$$

$$E = 64 \times \frac{220}{220} \times 0.0935 + 124 \times \frac{220}{220} \times 0.1875 = 6 + 23 = 29$$

1991 – 2000

APFO powder was no longer weighed so there was no exposure from this source.

$$AI_1 = 729 - (729 \times 0.1) = 656$$

$$AI_2 = \frac{656 \times 1}{1 \times 1 \times 1 \times 3} \times [(0.3 \times 1) + (0.7 \times 0.3)] = 112$$

$$E = 112 \times \frac{220}{220} \times 0.1875 = 21$$

Quality control

Exposures were determined independently by two occupational hygienists and compared and where similar the average of the two assessments was taken. Where there was a significant discrepancy (i.e. a correlation coefficient less than 0.8 and more than a two fold difference in ratios), each assessor checked their assessment and amended any calculation errors. Any remaining discrepancies were discussed and agreement reached on the appropriate corrective action to be taken. Care was taken to ensure that such corrective actions were consistent with other assessments.

During the assessment process roughly 5% of TFE and APFO assessments were repeated by the first assessor, blind to the original assessment result. This quality assurance was undertaken to ensure the reliability of the assessments.

References

Cherrie JW, Schneider T, Spankie S, Quinn M (1996). A new method for structured, subjective assessments of past concentrations. Occup Hyg 3: 75-83

Cherrie JW (1999). The effect of room size and general ventilation on the relationship between near and far-field concentrations. Appl Occup Environ Hyg: 539-546

Semple S (2002). GeoParkinson Study. Exposure assessment methodology. University of Aberdeen.

Appendix 1 – calculation of PPE multipliers

The mean surface area by body part for an adult male in is given in table A1 (ECETOC, 2001*).

Table A1 – Mean surface area by body part

Body part	Surface area (m^2)
Head	0.118
Trunk (inc. neck)	0.569
Upper arms	0.143
Forearms	0.114
Hands	0.084
Thighs	0.298
Lower legs	0.207
Feet	0.112
Mean total	1.645

* ECETOC, *Exposure factors source handbook for European populations (with focus on UK data*, 2001, Technical Report No. 79.

The area of the body covered by various items of clothing is shown in table A2.

Table A2 – Area of body covered by clothing

Clothing	Area	Area covered (m^2)	Proportion
Overalls	thighs + lower legs + upper arms + lower arms + (trunk – neck)	1.28	0.78
Gloves	hands +1/2 x forearms	0.14	0.09
Rubber boots	feet + ½ x lower legs	0.22	0.13

The assumed protection factors are given in table 3.

Table A3 – Assumed protection factors

Type of PPE	Protection factor (%)
Overalls	80
Gloves	90
Rubber boots	80

The overall protection offered by each item of PPE and for any combination of items can then be calculated.

For example, overalls cover 0.66 of the body surface area and offer a protection of 80%, protection over the whole body is thus 0.78 x 80 = 62%, i.e. exposure is reduced by a factor of 0.38

Similarly, multipliers can be calculated for a combination of PPE. For example, if overalls and gloves are worn, protection is given by:

$$0.78 \times 80 + 0.09 \times 90 = 70\%$$

The multiplier is therefore 0.30.