Removal of chemical contamination from vehicles: A comparison of weathering and active clean-up processes

Denys Amos and Brian Leake

DSTO, Materials Research Laboratory, P.O. Box 50, Ascot Vale, Victoria 3032 (Australia)

Abstract

The concentrations of chemical contamination desorbing from alkyd and polyurethane painted vehicles after exposure to sun and wind under winter conditions have been measured. A computer model has been used to determine the residual contamination level after weathering. The removal efficiency under winter conditions is compared with that under summer conditions and is shown to be approximately one eighth as effective. The weathering process is also compared with active clean-up processes involving detergent/steam and C8 emulsion/steam. The combination of C8 emulsion and steam is shown to be the most effective decontamination process.

1. Introduction

The manufacture of chemicals and the associated chemical industry are indispensable parts of our industrial society. This has been referred to as "The Chemical Age" [1]. The enormous use of chemicals is not without risk. Many chemicals are toxic to some extent and some are extremely hazardous. With increased usage the possibility of an accidental release also increases and even with excellent safety precautions accidents will occur as a result of equipment failure and human error. Transport in particular poses a major problem since the scope for accident is greatly increased. Considerable effort is expended in cleaning up spills from accidents. Emergency workers frequently must wear chemical protective suits and respirators as protection against toxic vapours. Processes which accelerate the reduction and removal of contamination will reduce the need for clean-up and also will reduce the time spent in protective clothing.

Correspondence to: Mr. D. Amos, DSTO, Materials Research Laboratory, P.O. Box 50, Ascot Vale, Victoria 3032 (Australia).

In a previous study [2] we examined the removal of contamination from vehicles through the natural processes of weathering by sun and wind during the summer months in South Eastern Australia. We concluded that weathering in summer months would be sufficient to reduce the hazard to below the minimum risk value for all but the most toxic of chemicals. In the present study we examine the processes of weathering during the cooler winter months and compare the efficiencies of clean-up procedures using active chemicals and physical processes.

2. Experimental

2.1 Desorption chamber

The chamber in which the studies were carried out was constructed of stainless steel and was thermally insulated and temperature controlled. Total volume of the chamber was 93 m^3. Mechanical circulation of the air inside the chamber ensured rapid mixing of desorbing vapour. Methyl salicylate (MS) was chosen as a simulant because of its intermediate volatility.

2.2 Analysis

MS vapour concentrations were monitored by sampling into propylene glycol in sequential sampler bubblers. The sequential samplers each held 12 bubblers containing 5 mL propylene glycol as the absorbing medium and were programmed to sample the chamber over a 24 or 40 hour time span. The bubbler contents were analysed subsequently for MS by UV spectroscopy.

2.3 Vehicles

The vehicle chosen was the in-service Landrover complete with canvas canopy and rubber tyres. We investigated two paint systems; (i) in-service matt olive drab alkyd paint and (ii) low gloss olive drab aliphatic poly-urethane paint (PUP) to GPC-P 154/3 [3].

MS containing Orasol Brilliant Fast Red (0.1%) and Tinopal SWN Conc (0.1%), as visual and fluorescent tracers respectively, was sprayed onto the side, front and windscreen of the Landrover from a hand-held pressurised sprayer. The contamination density was determined by collection of sprayed MS on felt pads (100 mm × 100 mm); after contamination these were removed for analysis. The quantity of MS on the felt pads was determined by ethanol extraction and spectrophotofluorimetric analysis of the Tinopal SWN tracer in the extract. The contamination process resulted in a fairly even distribution of simulant spread over the surface of the vehicle. In real accidents there may well be heavy and more localised contamination of the vehicle.

The contaminated vehicle was driven into the sealed chamber which was temperature controlled at 20 ± 1 °C. MS desorbing from the vehicle was monitored by collection for later analysis in four sets of sequential samplers arranged around the vehicle. Analysis of all data about the desorption of MS

from vehicles in the chamber was carried out using CONSAM which is the interactive version of the SAAM modelling program and allows the user to develop mathematical models to fit experimental data [4]. All data sets have been normalised to a contamination density of 10 g m^{-2} for purposes of comparison.

2.4 Clean-up processes

In the studies on weathering, the contaminated vehicles were exposed to sun and wind under Melbourne winter conditions during August and September for 90, 135 and 180 minutes to enhance removal of contamination. The mean insolation was 0.34 kW m^{-2}, mean wind speed 1.45 m s^{-1} and mean surface temperature 11 °C.

Two active decontamination processes were investigated, a physical removal system and a chemical destruction process. The physical removal system involved a pre-wash of the vehicle for 5 minutes with degreasing detergent (0.1%) in hot water at 60 °C followed by treatment with steam at 150 °C for 5 minutes. The active chemical decontamination process consisted of a pre-wash for 5 minutes with a degreasing detergent (0.1%) in hot water at 70 °C, followed by C8 decontaminant. This was applied by spraying and allowed to remain on the vehicle for 20 minutes; the C8 was finally removed by steam treatment at 150 °C. Hot water, detergent and steam were supplied in both instances from a portable steam generating unit, NBC-Sanator. C8 emulsion is an active chlorine military decontaminant containing calcium hypochlorite, tetrachloro-ethylene, an emulsifier and water [5].

3. Results and discussion

In previous studies [2, 6] Amos et al. developed a computer model to describe the desorption of a liquid chemical from vehicles in an enclosed chamber. The model described was

$$Ct = P_1 \left[1 - \exp(-P_2 (t - P_4)^{P_3}) \right] \tag{1}$$

where P_1, P_2, P_3 and P_4 are constants that have to be evaluated. Previous studies [2, 6] have shown that P_1 is related to the contamination level of the simulant, P_2 is an estimate of the desorption rate constant, P_3 is a measure of deviation from linear kinetics and P_4 is an offset allowing for errors associated with recording early observations for the experiment.

To establish the relationship between the initial contamination level (*IC*) of MS and P_1, three levels of simulant contamination were studied for each of the two painted vehicles. The vehicles were not subject to weathering or decontamination in this series and were placed in the chamber immediately after contamination. The experimental data were fitted to the model and the values
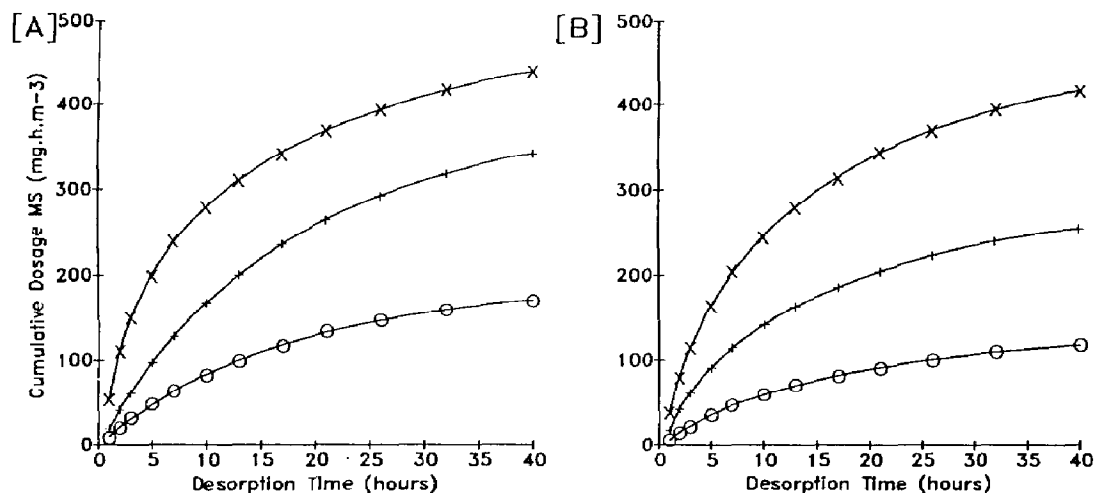
Fig. 1. Cumulative desorption of MS from [A] Alkyd vehicles and [B] PUP vehicles after winter weathering—experimental data and SAAM fits. The unbroken lines are the SAAM fits. Weathering time: ($\times$) 1.5 h, (+) 2.25 h, and ($\bigcirc$) 3.0 h.

of P_1 for each level of IC calculated. P_1 was regressed on IC and the following relationship was established:

$$P_1 = 5.2IC + 1.7 \tag{2}$$

3.1 MS desorption after weathering

The MS desorption data from vehicles exposed to the weather for various periods of time were fitted using CONSAM to the developed empirical model (eq. 1) as shown in Fig. 1. Values of P_1 calculated with eq. (1) are given in Table 1. Values of IC_w, the contamination level after weathering, are also detailed in Table 1 and were calculated from eq. (2).

TABLE 1

Derived values of P_1, level of residual contamination (IC_w) and removal efficiencies (RE) for MS after weathering under winter conditions for alkyd and polyurethane coated vehicles

Paint type	Weathering time (hours)	P_1 (S.D.)[a]	IC_w (g)	RE[b] (%)
Alkyd	1.5	540 (9.5)	104	18
Alkyd	2.25	396 (1.1)	75.6	41
Alkyd	3.0	197 (4.3)	37.6	70
PUP	1.5	487 (8.5)	93.1	27
PUP	2.25	306 (3.0)	58.5	54
PUP	3.0	141 (4.7)	26.8	79

[a] Standard deviation.
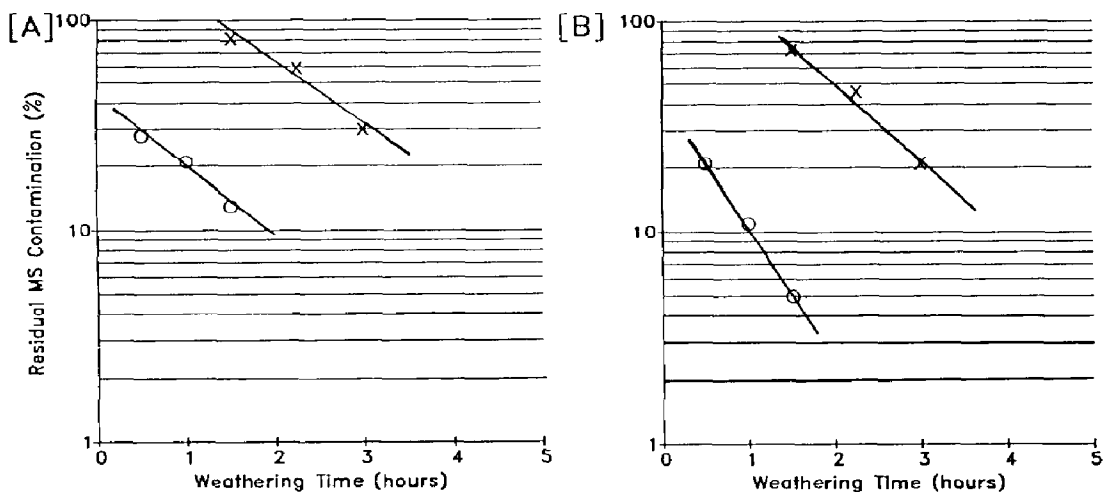[b] Mass of MS applied by spraying ($IC_0 = 127.5$ g).

Fig. 2. Plot of percentage residual MS contamination vs. weathering time for winter (×) and summer (○) months for [A] Alkyd vehicles and [B] PUP vehicles.

It is clear that weathering during winter months is not effective in removing MS contamination from the vehicles under examination. Removal efficiencies ranged from 18% to 70% for alkyd coated vehicles and 27% to 79% for polyurethane coated vehicles. The removal efficiencies for winter weathering are shown graphically in Fig. 2 and are also compared with data previously obtained from summer weathering [2]. The residual contamination levels after winter weathering are such that the hazard from many toxic chemicals would remain well above the minimum risk value of 3%. The consequence is that active means of decontamination or clean-up should be sought during winter months.

The polyurethane coating was designed to be extremely resistant to penetration by toxic chemicals and the greater removal efficiency for vehicles with such coatings may be attributed to the chemical hardness of the paint. That the removal efficiencies for the polyurethane systems are only some 10% greater than for alkyd systems may be ascribed to the penetration of MS into cracks and crevices and into other absorbent materials on the vehicles. Desorption from such design artifacts tends to negate the chemical hardness of the polyurethane paint.

3.2 Active clean-up process

Of the two decontamination procedures investigated, one relies upon physical removal, the other upon chemical destruction. In the former, treatment with a hot water and detergent pre-wash removes liquid contamination and any dirt, oil and grease which may have absorbed contamination. This is followed by application of steam at 150 °C which evaporates remaining liquid agent, accelerates the evaporation of absorbed contamination and contributes to destruction of contamination through hydrolysis.
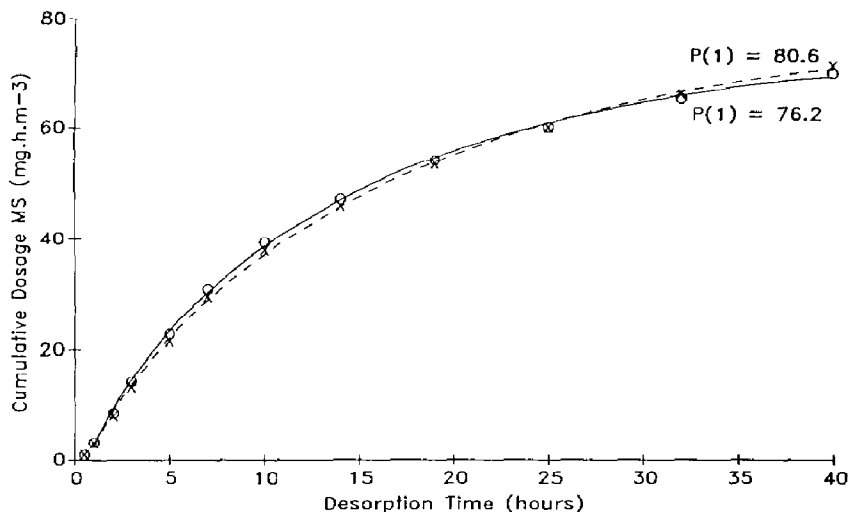
Fig. 3. Cumulative desorption of MS from vehicles after clean-up with a detergent pre-wash and steam at 150 °C—experimental data and SAAM fits. The solid and dotted lines are the SAAM fits, (○) PUP landrover, and (×) Alkyd vehicles.

Figure 3 depicts the desorption of MS from vehicles following treatment with detergent pre-wash and steam at 150 °C. The derived values of P_1, level of residual contamination (IC_w) and removal efficiencies (RE) for MS are detailed in Table 2.

The RE for MS on both vehicles is approximately 80% which is similar to that obtained by weathering during winter months for polyurethane vehicles and some 10% better than alkyd vehicles. There is little difference between the

TABLE 2

Derived values of P_1, level of residual contamination (IC_w) and removal efficiencies (RE) for MS after decontamination with detergent/steam or C8 emulsion/steam for alkyd and polyurethane coated vehicles

Paint type	Decontamination process	P_1 (S.D.)[a]	IC_w[b] (g)	RE (%)
Alkyd	Detergent steam	80.6 (2.7)	15.2	81
Alkyd	C8 emulsion steam	22.7 (0.5)	4.04	95
PUP	Detergent steam	76.2 (2.1)	14.3	82
PUP	C8 emulsion steam	20.1 (0.5)	3.42	96

[a] Standard deviation.
[b] Mass of MS applied by spraying ($IC_0 = 80$ g).

two types of paint system which indicates that the residual contamination is not associated with the paint systems but rather with common absorbing micro features.

3.3 Chemical decontamination process

The chemical decontamination procedure involves a pre-wash, as described above, followed by application of C8 emulsion, an active decontaminant which has been designed to extract extremely toxic contamination from absorbent surfaces into the emulsion where a combination of oxidation and hydrolysis ensures decomposition.

Finally the emulsion is removed by application of steam at 150 °C. The disadvantages of the system are the deleterious effects on some materials and possible problems associated with using chlorinated hydrocarbon solvents.

Figure 4 depicts the desorption of MS from vehicles following decontamination with C8 and steam at 150 °C. The derived values of P_1, level of residual contamination (IC_w) and removal efficiencies (RE) for MS are given in Table 2. RE for both types of painted surface is 95–96% with little difference between the two types of surface. As with the physical removal system the residual contamination is associated with micro design features of the vehicles.

Furthermore, the residual amounts of MS after decontamination with C8 are 4% and 5% for PUP and Alkyd vehicles. If we extrapolate the data depicted in Fig. 2 for summer weathering from these levels, then a level of 3% residual contamination would be reached 0.5 to 1 hour after completion of the decontamination process i.e. 1 to 1.5 hours after contamination. In this regard the C8 process must be regarded as more effective than summer weathering.
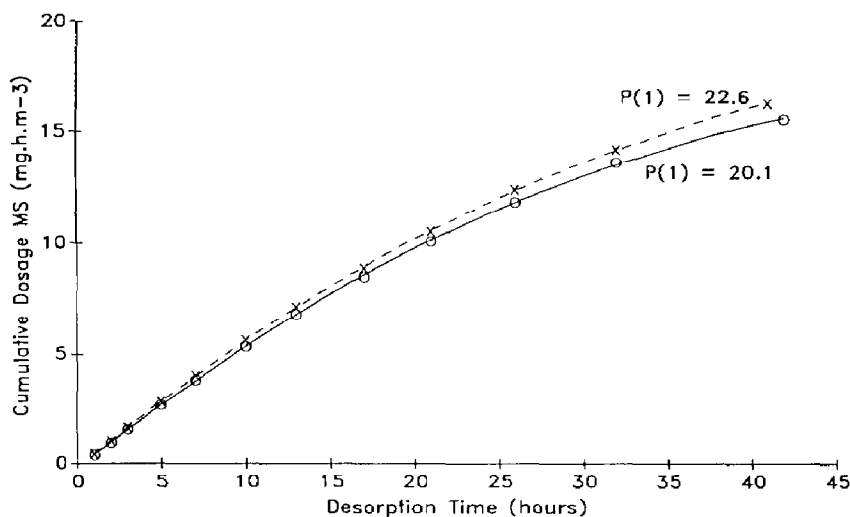

Fig. 4. Cumulative desorption of MS from vehicles after decontamination with C8 emulsion and steam at 150 °C—experimental data and SAAM fits. The solid and dotted lines are the SAAM fits, (○) PUP landrover, and (×) Alkyd landrover.

Decontamination with the C8 process therefore is necessary to eliminate vapour hazard in cooler climates or in winter conditions similar to those in S.E. Australia.

4. Conclusions

With summer weathering a level of 3% residual contamination would be achieved by weathering for 2–4 hours depending on paint type. This would be sufficient to reduce the hazard to below the minimum risk value for most chemicals. Weathering during the winter would not be sufficient to reduce the vapour hazard to minimum risk levels.

The physical removal system, while more effective than winter weathering, also did not reduce the residual vapour hazard to below the minimum risk value.

The C8 emulsion system is much more effective than either the physical removal system or winter weathering in removing contamination. The C8 process also must be regarded as more efficient in combination with weathering than summer weathering alone. It is necessary to eliminate vapour hazard in cooler climates or in winter conditions similar to those in S.E. Australia.

References

1   H.D. Crone, Chemicals and Society: A guide to the new chemical age. Cambridge University Press, Cambridge, 1986.
2   D. Amos, R.C. Boston, P.J. Gray and B. Leake, J. Hazardous Materials, 23 (1990) 203–214.
3   GPC-P-154/3. Paint, Polyurethane, Olive Drab, Lustreless, Two Pack. Government Paint Committee Specification: Dept. Admin. Affairs, Port Melbourne, Vic., 1989.
4   M. Berman, W.F. Beltz, P.C. Greif, R. Chabay and R.C. Boston, CONSAM Users Guide, Laboratory of Mathematical Biology, National Cancer Institute, National Institute of Health, Bethesda, MD, 1983.
5   A.M.H. Chang and A. Ciegler, NBC Defence Technol. Int., 1(4) (1986) 59–65.
6   D. Amos, B. Leake and R.C. Boston, J. Environ. Sci. Health, (1992), in press.