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CO-DISTILLATION OF AGENT ORANGE AND OTHER PERSISTENT ORGANIC POLLUTANTS IN EVAPORATIVE WATER DISTILLATION

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Introduction

Human exposure to polychlorinated dibenzodioxins and dibenzofurans (PCDD/Fs) is primarily attributed to the consumption of contaminated food¹. This is due to the physical chemical properties of these compounds including their persistence through the food chain and their hydrophobicity². Usually, contamination of drinking water is not considered a relevant pathway for these chemicals to humans due to the low water solubility and exceptionally high sorption coefficients of PCDD/Fs. On ships, within island communities and in arid areas, potable water is sometimes produced by evaporative distillation from seawater. This study arose from a desire to understand results published by the Australian Department of Veterans' Affairs, that showed a slight increased overall mortality of male Vietnam veterans between the years 1980 and 1994³. In that report, it was noted that veterans of the Royal Australian Navy (RAN) experienced higher mortality than other Australian Vietnam Veterans. However RAN personnel were, in the main, deployed on ships that were on coastal patrols off Vietnam or transporting troops and materials from Australia to Vietnam. Foodstuffs on ships were sourced from Australia, and sailors only occasionally landed in Vietnam, and then only for short periods. No record can be found of an Australian ship being sprayed with herbicide. Thus, we could see little possibility for exposure of RAN personnel to herbicides and associated contaminants, except via the water supply. For the supply of fresh water on board the vessels, water from the surrounding marine or estuarine environment was distilled using evaporative distillation units. The vessels were often in water which seem likely to have been contaminated with residues from the spraying of inland and coastal areas.

The aim of this study was to assess the potential for PCDD/Fs to co-distil during the distillation of contaminated water. Here we report some of the results of the study and discuss their implications on the use of distillation as a means for purification of water.

Methods and Materials

In distillation plants on RAN ships seawater was usually fed into an evaporator where the water was boiled by a combination of heating and reduced pressure (vacuum). The vapour was condensed in the condenser from where it was pumped into the feed tanks (for details see reference⁷). The distillation units of the ships operate in essence similar to a rotary evaporator unit used in laboratories. Therefore, the following experimental setup was designed for this study: Clean one-litre round bottom flasks were spiked with native PCDD/F standards to obtain a

pollutant concentration in the water between 10 and 60 ng/L of selected tetra- to octachlorinated congeners and 100-200 ng/L of a range of chlorinated pesticides (Table 1).

(Note that for the organochlorines and the lower chlorinated PCDD/Fs the compound concentration was substantially below the solubility of the chemicals in the water). The solvent of the spike solution was evaporated before water was added. Treatments of the experiments included three salinity concentrations (0, 15 and 30 g/L) and at 30 g/L NaCl concentration, four levels of total suspended solids (TSS) (0, 0.2, 0.6 and 1.8 g TSS/L). The NaCl and TSS was added with the water then the flasks were wrapped in aluminium foil, and shaken for at least a week, ensuring that the chemical could equilibrate between the surface of the container, and the water.

Table 1 Water solubility, concentrations of spike and relative retention times (RRT) of investigated compounds. Water solubility data compiled from Refs⁴⁻⁶.

Compound	Aqueous solubility	Spike ng/L	RRT
HCB	5 ug/L	100	0.36
Lindane	2.2 – 10 mg/L	100	0.50
Heptachlor	6 – 200 ug/L	100	0.54
Heptachlorepoxyde	20-200 ug/L	100	0.59
Aldrin	10-200 ug/L	100	0.73
Dieldrin	20-2000 ug/L	100	0.82
DDT	1-460 ug/L	200	0.86
DDE	1-55 ug/L	200	0.98
DDD	2-160 ug/L	200	1.02
2,3,7,8-TCDD	8-200 ng/L	40	0.99
1,2,3,4-TCDD	640 ng/L	8.6	1.14
1,2,3,7,8-PeCDD	120 ng/L	40	1.18
1,2,3,4,7,8-HxCDD	4.4 ng/L	40	1.36
1,2,3,4,6,7,8-HpCDD	2.4 ng/L	40	1.61
OCDD	0.074-0.4 ng/L	60	1.96
2,3,7,8-TCDF	419 ng/L	40	1.00
1,2,3,7,8-PeCDF	236 ng/L ^b	40	1.14
1,2,3,6,7,8-HxCDF	17.7 ng/L	37	1.31
OCDF	1.4 ng/L	61	1.95

The three fractions were subject to liquid-liquid partitioning, twice using dichloromethane and for a further time using hexane. The non-polar fractions were combined, concentrated to almost dryness and then topped up with 20 µl of toluene. Initially, samples were analysed without a clean-up, which resulted in a variety of chromatography problems as well as low sensitivity and interferences with the mass spectrometry in selected samples. Hence a clean-up using acid/base (H₂SO₄ and KOH) impregnated silica gel and aluminum oxide in series was carried out in

subsequent treatments. Samples were eluted using hexane:dichloromethane (1:1), the eluent was evaporated and the samples were transferred into vials, concentrated and filled with 20 μ L toluene. Analyses of PCDD/Fs and organochlorines was performed on a gas chromatograph (Shimadzu GC17A, DB-5 fused silica column, 30 m, 0.25 mm i.d., 0.25 μ m film thickness) interfaced to a Shimadzu QP5050 mass spectrometer operating in selective ion monitoring mode.

Organochlorines and PCDD/Fs were identified using retention times in the standard solution and evaluation of correct isotope ratios M^+ and M^{2+} . Quantification was undertaken by external calibration against the standards that were used to spike the samples. (Note that the study did not require absolute quantification of the concentrations since the aim was to evaluate the relative proportions of the chemicals of interest in various fractions of the distillate).

Results and Discussion

The relative quantity of the chemicals of interest in the first distilled fraction (F1) from RO water compared with the concentration in a control ranged from 113 % to about 13 %. None of the chemicals of interest were detectable in any of the blank samples. An example of co-distillation for individual compounds in RO water is shown in Figure 1. Co-distillation was highest for the organochlorine pesticides (Fig. 1a) and lower chlorinated PCDD/Fs (Fig. 1b). The results demonstrated that if the compounds are dissolved in pure water almost the entire quantity of chemicals such as hexachlorobenzene, heptachlor or gamma hexachlorohexane and about 73 - 85 % of the DDTs co-distil with the first 14 % of water. For the polychlorinated dibenzodioxins and dibenzofurans a trend of decrease in co-distillation with an increase in chlorination was apparent in the first 14% of distillate and the relative retention time (RRT see Table 1) of the chemicals provided a useful descriptor that correlates with the degree of co-distillation in this study. Interestingly in this first experiment 2,3,7,8-tetrachlorodibenzodioxin, considered the most toxic of all PCDD/Fs and the main contaminant in Agent Orange, was found at about 85 % of the quantity observed in the control samples and co-distilled to a greater extent than any other PCDD/F investigated here. In contrast, about 10 – 20 % of the hepta- and octachlorinated PCDD/Fs were found in the distilled fraction in the first experiment. These results indicate that distillation of only a fraction of water (a common practice when saline water is distilled for drinking water on ships) will result in a substantial concentration increase of all investigated organochlorine pesticides as well as TCDD/Fs and other lower chlorinated PCDD/Fs.

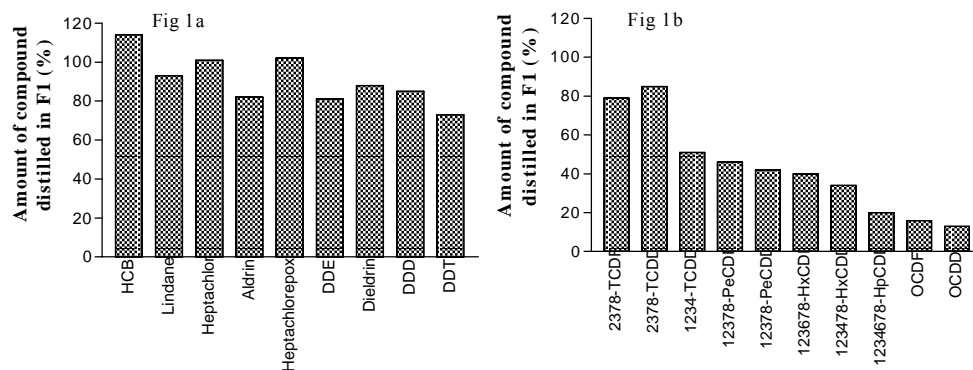


Figure 1. Co-distillation of organochlorines (Fig. 1a) and PCDD/Fs (Fig 1b) from pure RO water when 14.1 % (141 mL of 1000 mL) was distilled. The values represent the quantity in the samples' distillate relative to the total quantity in a control of spiked but non-distilled water.

No significant change in co-distillation with an increase in NaCl concentration in the water could be observed, although a trend of increasing co-distillation with an increase in the NaCl level was indicated by the data. Addition of suspended solids in the form of dried sediments resulted in a decrease of the level of co-distillation compared to RO water. However it was interesting to note that even at a concentration of 1.8 g total suspended solids (which is in excess of the TSS concentration in most estuarine systems) about 40 % of the 2,3,7,8-TCDD co-distilled with the initial 9 % of distilled water (Figure 2).

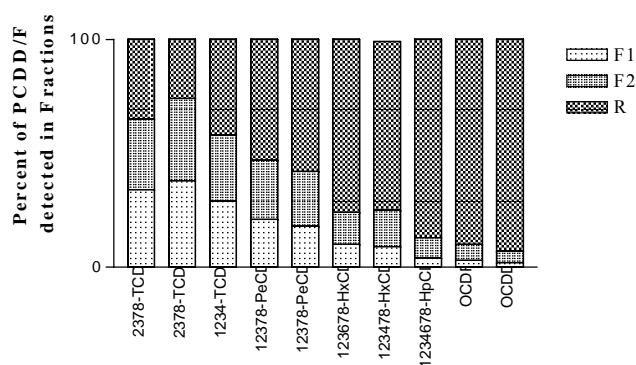


Figure 2. Co-distillation of PCDD/Fs from water containing 30 g/L NaCl and 1.8 g/L of TSS. F1 comprised of 9 % and F2 of a further 30 % of the initial water to be distilled.

The results from this study demonstrate that evaporative distillation may allow TCDD and other persistent semivolatile organic chemicals to enter water supplies and to concentrate in the distillate. Thus, if distillation is used for obtaining potable water it needs to be ensured that the source water is not contaminated. With respect to Vietnam veterans that served with the Royal Australian Navy this study provides evidence that contamination via water may have been an important pathway for contamination of personnel with TCDD on board ships.

Acknowledgments

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References

1. Liem, DAK, Fuerst, P, Rappe C (2000) Food Additives and Contaminants 17, 241.
2. McLachlan, M. (1996) In Issues in Environmental Science and Technology R. E. Hester, R. Harrison, M, Eds. The Royal Society of Chemistry, Cambridge UK, 1996, Vol. 6, 31.
3. CraneP, Barnard j, Horsley KW, Adena MA. (1996) A report of the 1996 Retrospective Cohort Study of Australian Vietnam Veterans Department Veterans Affairs, Canberra, Australia.
4. Mackay D, Shiu W, Ma KN. (1992) Illustrated handbook of physical-chemical properties and environmental fate for organic chemicals Vol 2. Aromatic hydrocarbons and polychlorinated dibenzofurans and dibenzodioxins Lewis Publisher, Chelsea, Mi., USA.

5. Hülster, A. (1994) PhD Thesis University of Hohenheim.
6. IARC (1997) Polychlorinated dibenzo-para-dioxins and polychlorinated dibenzofurans
In: IARC Monographs on the evaluation of carcinogenic risks to humans. IARC, Lyon, France
7. Ship Department Admiralty (1966) Naval Marine Engineering Practice Volume 1, Her Majesty's Stationary Office, London.