Control No. AM355

PARTITION COEFFICIENTS OF SOME NIAGARA RIVER ORGANIC CONTAMINANTS

by

D.H.J. Anthony and P.D. Goulden

Analytical Methods Division

National Water Research Institute

Canada Centre from Inland Waters

Burlington, Ontario L7R 4A6

NWRI Contribution No. 86-222

MANAGEMENT PERSPECTIVE

This collection of octanol-water partition coefficients for a number of organic materials completes the documentation of the design basis of the large-sample extractor currently being used to monitor organics in the Niagara River and Great Lakes.

PERSPECTIVE DE GESTION

Cet ensemble de coefficients de partage d'octanol-eau pour plusieurs composés organiques vient compléter la documentation qui constitue la base de conception de l'extracteur de gros échantillons que l'on utilise à l'heure actuelle pour surveiller les composés organiques dans le Niagara et dans les Grands Lacs.

ABSTRACT

Partition coefficients of a number of organic materials for the octanol-water system have been collected from the literature. The organic materials are those being monitored in the Niagara River and elsewhere in the Great Lakes. The partition coefficient is the basic parameter necessary for design of solvent extraction equipment. This collection completes the report of the design basis for the large-sample extractor being used by the Water Quality Branch for monitoring purposes.

INTRODUCTION

One route to low detection limits in the determination of organics in water is the use of a large-volume sample, from which the organics are extracted with solvent. A co-operative programme to develop convenient and low-cost equipment for this purpose has been carried out by the Water Quality Branch and the National Water Research Institute. In this work a continuous-flow large-sample extractor has been developed which extracts water sample flows of up to 1 L per minute. With this equipment it has been possible to handle, on a routine basis, samples of 50 litres or more. The design basis for this extractor has been described (Goulden and Anthony, 1985) as has the operation of the shipboard version used to monitor the Great Lakes (Nielson et al., 1987). Other versions of the extractor are being used to monitor the Niagara River. (Reports on these are in preparation).

The key parameter in the design of solvent extraction equipment is the partition coefficient of the materal of interest between the solvent and water. In the above design report (Goulden and Anthony, 1985), the relationship between the partition coefficient and the theoretical extraction efficiency is discussed. The claim is made that the partition coefficients are large enough for extraction to be complete but no specific values are given. The present work is intended as an addendum to this report; it collects together from the literature partition coefficients of materials required to be

determined in the monitoring programmes carried out by the Water Quality Branch. The list of organic contaminants that are being monitored in the Niagara River is large and comprehensive (Niagara River Toxics Committee, 1984); it has been used as the basis in compiling the attached tables. In addition are given the partition coefficients for materials known to be of interest in other monitoring programmes and for the surrogate standards that are added to the water samples before the extraction in order to provide a continuing measure of the extraction efficiency.

RESULTS AND DISCUSSION

The solvent used to extract the organics from the water sample is dichloromethane (DCM). Unfortunately, partition coefficient data for the dichloromethane-water system are very meagre in the literature. The solvent system for which there are data available for most organics is the octanol-water system. This is because of their application in the study of Quantitative Structure-Activity Relationships (QSAR). As previously discussed (Goulden and Anthony, 1985), it is believed that the partition coefficients for the dichloromethane-water system are not very different from those of the octanol-water system and for most of the organic materials of concern the DCM system values are probably higher. In Table I are shown the values of the partition coefficients in the octanol-water system for the contaminants of interest, together with the values for four of the five surrogate standards added to each water sample extracted. In

Table II are given the values in the octanol-water and dichloromethane-water systems for those compounds for which this information is available; most of these compounds have no significance in the monitoring programmes.

It has not been possible to find partition coefficient values for all the materials of interest. Two of particular interest are TCDD (2,3,7,8-tetrachlorodibenzo-p-dioxin), a particularly toxic contaminant, and endrin ketone, one of the surrogate standards added to the water samples. Limited work using Cl^{37} substituted TCDD has shown that its extraction from Great Lakes water is complete; for the several hundred natural samples to which endrin ketone has been added, the recovery has averaged 100%. These results indicate that the partition coefficients for these two materials are log 4 or higher.

It must be remembered however that these partition coefficients are for liquid-liquid systems and take no account of the particulate and colloidal material that may occur in natural water samples (even after filtration or centrifugation) to which the organics may be adsorbed. Work using the large-sample extractor with a variety of water samples has given some qualitative indications of the particulate-solvent partition coefficient and, perhaps more importantly, the kinetics of the extraction from the particulates. It is concluded that the liquid-liquid partition coefficients do provide a reasonable basis for the design of solvent extraction equipment but that a considerable amount of work with actual water samples is necessary before it can be shown that the process is a valid one.

ACKNOWLEDGEMENT

We would like to thank Dr. Barry Oliver (ECD/NWRI) for his assistance in providing us with several of the literature references cited in Tables I and II.

REFERENCES

Goulden, P.D. and D.H.J. Anthony. 1985. Design of a large-sample extractor for the determination of organics in water. NWRI Contribution No. 85-121.

Neilson, M., R. Stevens, H. Biberhofer, P.D. Goulden and D.H.J. Anthony. 1987. A large-sample extractor for determining organics in the Great Lakes. IWD Report (in press).

Niagara River Toxics Committee, 1984, Report of the Niagara River Toxics Committee.

Table I Partition coefficients for octanol-water system.

Compound	Log K_{ow}	Reference
NRTC Group I Organic Contaminants		
1. TCDD	(>4, see text)	-
2. Aldrin	3.01	1
3. Alpha BHC	3.9	4
	3.81	9
4. Alpha chlordane	6.0	2
	2.78	9
5. Gamma chlordane	6.0	2
6. p,p'-DDD	6.02	3
	5.99	9
7. p,p'-DDE	5.69	2
8. p,p'-DDT	5.75	2
	3.98-6.19	9
9. Dieldrin	-	-
10. Alpha endosulfan	3.55	9
11. Beta endosulfan	3.62	9
12. Endrin	4.56	3
13. Heptachlor	5.44	2
14. Heptachlor epoxide	5.40	2
15. Hexachlorobenzene	5.50	5
16. Hexachlorobutadiene	4.9	6
17. Lindane	3.72	1
	3.89	2
18. Methoxychlor	4.30	1
19. Benzo (B) fluoranthene	6.57	9
20. Benzo (K) fluoranthene	6.84	9
21. Benz (A) anthracene	5.61	9
22. Benz (A) pyrene	6.50	7
23. Chrysene	5.91	7
24. Fluoranthene	5.22	7
25. Pyrene	4.88	1
	5.22	7
26. Arochlor 1242	5.58	3
27. Arochlor 1254	6.47	2
28. Arochlor 1260	6.91	2
29. Pentachlorophenol	5.12	1
	5.01	2
30. Phenol	1.48-1.51	1
31. 2,4,5-Trichlorophenol	3.72	3
32. 2,4,6-Trichlorophenol	3.62-4.05	1
33. Bis (2-ethylhexyl) phthalate	4.20	2
	5.3, 8.73	9

34. Dioctylphthalate	9.2	9
35. Benzene	2.04-2.15	1
36. Carbon tetrachloride	2.83,2.62	1
	2.64	2
37. Chloroform	1.97,1.94	1
38. 1,1-Dichloroethane	1.48	1
39. Methylene chloride	1.25	1
40. Tetrachloroethene	2.60	1
	2.88	2

Additional Compounds

PCB's	3-8	8
Octachlorostyrene	6.29	2
Mirex	6.89	2
1,2-Dichlorobenzene	3.55	7
1,3-Dichlorobenzene	3.60	7
1,4-Dichlorobenzene	3.62	7
1,2,3-Trichlorobenzene	4.11	7
1,2,4-Trichlorobenzene	3.93	7
1,3,5-Trichlorobenzene	4.15	7
1,2,3,4-Tetrachlorobenzene	4.46	7
1,2,3,5-Tetrachlorobenzene	4.50	7
1,2,4,5-Tetrachlorobenzene	4.52	7
Pentachlorobenzene	4.88	7
Toxaphene	3.3	9
Naphthalane	3.36	1
Biphenyl	4.09	1
2-Methylnapthalene	4.11	1
Phenanthrene	4.57	1
Anthracene	4.54	1
	4.45	9
Dimethylphthalate	2.11	1
Diethylphthalate	3.15	1
Beta - BHC	3.78	1
	3.80	9
Delta - BHC	4.14	1

Surrogate Standards

1,3-Dibromobenzene	3.75	1
1,3,5-Tribromobenzene	4.5	10
1,2,4,5-Tetrabromobenzene	5.1	10
Tetrachlorobiphenyl isomers	5.6-6.7	8
Endrin ketone	(>4, see text)	

Table II Some compounds for which comparative octanol-water (K_{ow}) and dichloromethane-water (K_{DCM-W}) have been found (reference (1)).

Compound	K_{DCM-W}	K_{OW}
N-nitroso-heptamethyleneimine	2.76	1.48
2,6-dimethyl-N-nitrosopiperidine	2.71	1.36
8-quinolinol (oxine)	2.58	1.96
amphetamine	1.8	1.76
2,4,6-trinitrophenol	2.07	2.03
	2.04	
4-methyl-N-nitrosopiperazine	0.79	0.2
acetylacetone	1.31	0.34
N-nitrosopiperazine	0.43	0.18
N-nitrosotrimethylurea	1.49	0.36
N-nitrosothiomorpholine	1.92	0.4
phenol	0.69	1.5
diphenylolpropane	1.3	3.32

REFERENCES FOR TABLES I AND II

1. Hansch, C. and A. Leo. 1979. Substituent Constants for Corelation Analysis in Chemistry and Biology, Appendix II, Partition Coefficients, pp 171-319, John Wiley and Sons, New York, NY. ISBN#0-471-05062-8.
2. Veith, G.D. et al., 1979. J. Fish Res. Board Can., 36, 1040-1048.
3. Veith, G.D. et al., 1979. Wat. Res., 13, 43-47.
4. Oliver, B. and M.N. Charlton, 1984. Environ. Sci. Technol., 18, 903-908.
5. Chiou, C.T. et al., 1982. Environ. Sci. Technol., 16, 4-10.
6. Chiou, C.T., 1985. Environ. Sci. Technol., 19, 57-62.
7. Bruggeman, W.A. et al., 1982. J. Chrom., 238, 335-346.
8. Rapaport, R.A. and S.J. Eisenreich, 1984. Environ. Sci. Technol., 18, 163-170.
9. Callahan, M.A. et al, 1979. Water-Related Fate of 129 Priority Pollutants, V.I & II, U.S. EPA# 440/4-79-029 a & b.
10. Wataral, H. et al., 1982. Anal. Chem., 54, 702-705.