SELECTION OF PCBs FOR LABORATORY TESTING OR USE AS INDICATORS IN ENVIRONMENTAL MONITORING

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1. INTRODUCTION

One important step in the design of experiments, often not given serious attention, is the representativity of the compounds investigated. If knowledge should be reached of a specific phenomena, the physico-chemical features of the class of compounds under investigation must be represented. The PCBs consist of a large number of possible congeners with varying degree of chlorination and substitution patterns. No single congener can be used as a structurally representative congener for the whole class of compounds and hence, a number of congeners have to be investigated in order to include the many facets of chemical structure within the PCBs. One criteria for selection could be the degree of chlorination, another the number of chlorine atoms in *ortho*-position. However, most physical or biological systems are complex, and it is unlikely that only a single or a few chemical properties will suffice to describe them. Thus, it is necessary to characterise the compounds with a multitude of physico-chemical descriptors describing their properties. It is expected that such a broad chemical characterisation will capture the underlying, hidden factors that correlate with the response of interest, and should be used as the base for selection of congeners for physical or biological testing.

In this paper we present a tool for selection of small representative sets, so called training sets, of PCB congeners for use in the design of laboratory experiments or use as indicator congeners in environmental monitoring. The numbering of the congeners is according to the IUPAC-system.

2. MATERIAL AND METHODS

Physico-chemical descriptors. The chemical properties of the PCBs were described with a multitude of physico-chemical parameters, altogether 47 different variables, see Table 1. These variables, which are considered to include electronic, steric and lipophilic factors, were used in a multivariate chemical characterisation of the PCBs. The specific variables and references for original data are presented elsewhere [1,2].

Aroclor mixture. A mixture of Aroclor 1232, 1242, 1248 and 1260 was analysed by HRGC/LRMS using a Fisons MD800 coupled to a Fisions GC8000. The GC column used was a 60m x 0.32mm i.d. Supelco PTE-5 capillary column (Bellefonte, PA, USA). The GC was temperature programmed, 180°C initial hold for 2 min, 15°C/min to 205°C, followed by 2°C/min to 300°C. Single elution congeners were identified and used in the procedure of selecting representative indicator congeners in environmental monitoring.

Table 1. The physico-chemical parameters used in the multivariate chemical characterisation of the tetra- through heptachlorinated PCBs[1,2].

Physico-Chemical Parameters	
Indicator variables ("1" or "0")	Isolated atomic energy
Total surface area	Electronic energy
Octanol/water partition coefficient	Core-core interaction energy
Henry's law constants	Heat of formation
Gas chromatographic retention times	Dipole moments (point charge)
Relative response factors	Dipole moments (sp-hybridisation)
Octanol/water partition coefficient	Sum dipole moments
Solubility parameter	Ionisation potential
No.of chlorine atoms in *ortho*-position	Electron affinity
Molecular polarisability	*HOMO-LUMO* gap
Total energy	Absolute hardness
Binding energy	Absolute electronegativity

Multivariate chemical characterisation. The systematic variation (information) in the physico-chemical data was extracted by principal component analysis (PCA) [3]. The calculations give a few orthogonal dimensions, expressing the different PCB congeners in so-called principal properties. Each principal property is a linear combination of several properties expressed in the original data.

Experimental design. A 2^4-factorial design (FD) was used in combination with the first four principal components from the PCA. Statistical designs [4], such as FD, produce well-balanced sets of compounds through distributing the congeners over the whole chemical domain, because it generates the set of congeners by varying all design factors simultaneously. FD have previously been used for selection of so-called training sets of polychlorinated dioxins and dibenzofurans [5,6].

3. RESULTS AND DISCUSSION

Representative tetra- through heptachlorinated PCBs. The PCA of the 154 tetra- through hepta-chlorinated PCBs resulted in a nine-dimensional model, explaining 84% of the variation in the data. The first four principal components (PCs) described 69% of the variance, viz. 39%, 13%, 10% and 7%, respectively. These first four PCs were used as design variables in a 2^4-FD. Congeners with similar physico-chemical properties will cluster together as expressed with the same sign of the PCs, respectively. Table 2 shows the 16 design levels generated by the 2^4-FD and the congeners on each design level. In addition, congeners with low values in the four PCs are suggested to be so-called center-points, representing the interior part of the design. In order to introduce systematic and representative chemical variation into research programmes, using chemical or biological experiments, at least one congener from each design level is suggested to be included. In this way the number of congeners needed to be tested are relatively low, the structural variation within the class of compounds are included, and the general information on the behaviour of all tetra- through heptachlorinated PCBs can be estimated. A selection of 20 congeners according to this experimental protocol is presented elsewhere [2].

Table 2. A multivariate characterisation of all the 154 tetra- through hepta-chlorinated PCBs. The principal properties in combination with a 2^4-full factorial design.

Design:				PCB-congener (IUPAC)
+	+	+	+	129, 130, 134, 137, 140, 142, 170, 171, 172, 173, 174, 176, 181
-	+	+	+	46, 50, 51, 62, 65, 86, 89, 94, 97, 102, 116, 125, 152
+	-	+	+	105, 114, 122, 123, 124, 126, 127, 156, 159, 160, 166
-	-	+	+	55, 60, 61, 77, 81, 85
+	+	-	+	133, 139, 144, 147, 148, 150, 151, 154, 155, 161, 175, 178, 179, 188
-	+	-	+	42, 53, 54, 92, 96, 101, 103, 104, 121
+	-	-	+	115, 118, 120, 138, 153, 158, 163, 169
-	-	-	+	49, 52, 63, 64, 68, 72, 74, 75, 79, 80, 111, 117, 119
+	+	+	-	128, 131, 132, 135, 141, 143, 145, 182, 185, 186
-	+	+	-	40, 41, 43, 45, 48, 82, 83, 87, 88, 93
+	-	+	-	180, 190
-	-	+	-	57, 67, 76, 78, 106, 108, 109
+	+	-	-	136, 146, 149, 165, 177, 183, 184, 187
-	+	-	-	44, 69, 73, 84, 90, 91, 95, 98, 100, 113
+	-	-	-	157, 162, 164, 167, 168, 189, 191, 192, 193
-	-	-	-	47, 56, 58, 59, 66, 70, 71, 99, 107, 110, 112
				Possible "center-point" congeners
0	0	0	0	99, 107, 108, 111, 112, 115, 116, 117, 153

Indicator PCBs representing a Aroclor mixture. A separate PCA was calculated for the 52 PCB congeners, on a Supelco PTE-5 column, single eluting PCB congeners in the Aroclor mixture. The calculations were based on the same previously used physico-chemical descriptors. A seven-dimensional model explained 88% of the variation in the data. The first four PCs explained 48%, 11%, 9%, and 6%, respectively. The principal properties were combined with a 2^4-FD and the different congeners distributed over the different design levels as decided by the sign of the four PCs, see Table 3. By selecting one congener from each design level, a set of representative congeners, for the Aroclor mixture, is achieved. These are suggested to be used as a small set of indicator congeners containing the structural variation found in the Aroclor mixture.

4. CONCLUSIONS

The use of multivariate chemical characterisation in combination with factorial design provide a tool by which small sets of structurally representative congeners can be selected. This tool should be used in the design of chemical or biological experiments in order to introduce systematic structural variation in the congeners tested. In studies of complex environmental mixtures of PCBs, indicator congeners can be selected from the structural variation found in Aroclor mixtures. The use of these systematic and balanced sets of congeners in the experimental protocol will provide increased knowledge of the environmental behaviour of the PCBs

Table 3. A 2^4-factorial design generating representative congeners in a Aroclor Mixture.

Design:				PCB-congener (IUPAC)
+	+	+	+	146, 183
-	+	+	+	52,91,110
+	-	+	+	151,199,201
-	-	+	+	44, 45, 49,101
+	+	-	+	128, 156, 180, 191, 194
-	+	-	+	66, 74
+	-	-	+	141, 185
-	-	-	+	33, 123
+	+	+	-	149, 168,178, 193
-	+	+	-	26, 27, 31
+	-	+	-	179, 197, 202, 209
-	-	+	-	19, 53
+	+	-	-	158, 171, 177, 206
-	+	-	-	22, 28, 42, 118
+	-	-	-	174, 176, 195, 200
-	-	-	-	17, 25, 51, 91
				Possible "center-point" congeners
0	0	0	0	149, 151, 168

5. ACKNOWLEDGEMENT

We gratefully acknowledge the Center for Environmental Research in Umeå (Grant 93257), the Swedish Environmental Protection Agency (Grants 30356 and 30418), and the Faculty of Mathematics and Natural Sciences, Umeå University, for financial support.

6. REFERENCES

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