EVALUATION OF PATTERNS AND SPATIAL TRENDS OF PESTICIDE RESIDUES FROM VIKUGE FARM, COAST REGION, TANZANIA BY PRINCIPAL COMPONENTS ANALYSIS

KF Kilulya and GS Mhinzi*
Chemistry Department, University of Dar es Salaam,
PO Box 35061 Dar es Salaam, Tanzania.
Corresponding authorl: gmhinzi@yahoo.com

ABSTRACT

This paper reports on the analysis of organochlorine pesticides pollution data obtained from samples collected from Vikuge farm, Coast Region, Tanzania between 2000 and 2003 by principal component analysis (PCA). PCA of the data sets for pesticide residues in water, soil and sediments samples from Vikuge has shown that the obsolete pesticides dumped at Vikuge pasture farm for a number of years undergo degradation with time and the distribution pattern of the pesticides in the three environments is similar. Strong outliers were also identified in the data by the use of PCA score plots. Further analysis of the data by the use of line plots has shown a decreasing trend of the concentrations of the pesticide residues with increasing distance from the point source (the place where obsolete pesticides were dumped). However, the data from sediment samples obtained from Vikuge farm has shown an increase of the residues concentrations with increasing distance from the nearest point to the area where the pesticides were dumped.

Keywords; Chemometrics, Principal Components Analysis, Pesticides

INTRODUCTION

As in all branches of science, and in analytical chemistry in particular, researchers depend on statistical measurements for reporting their results. This is due to the increasing demand for higher specificity and sensitivity that has been facilitated by developments in instrumentation and computer systems. The field of chemometrics is founded on the border between chemistry and mathematics/statistics. The most prominent part of chemometrics is data analysis and interpretation by multivariate methods. Chemometrics finds out the hidden relationships, which exist between the available data and the desired information. Usually Principal Components Analysis (PCA) is used in the evaluation of environmental data. It provides a deeper insight into frequently voluminous tables of data and combines the properties of a data table into a small number of new variables, called principal components (PC). These are selected in a way that they capture most of the information contained in the original data. Because of the smaller number of the PCs, it is much easier to display the data graphically in the PC coordinates and thus notice the features of the data. The output of the PCA is usually presented as score plots, which show the relationships among the samples, and as loading plots, which show the effects of the originally measured variables on the PCs. Samples, which have similar PCs are similar and variables which have similar loadings on a PC are correlated.

PCA decomposes a matrix of data, X, with N rows (observations) and p columns (variables) into a signal part and a noise part according to the equation:

$$\mathbf{X} = \mathbf{TP}^{T} + E$$

where TP^T is a matrix product of scores matrix T and loading matrix P, and E is the residual matrix which contain noise/residuals (Eriksson *et al*. 1999, Geladi *et al*. 1989, Wold *et al*. 1984a).

One of the most important tasks in using PCA is determining the correct number of principal components. The PC residuals, $e_{ik,}$ decrease when the number of parameters increases, i.e. when the number of significant principal components (PC) increases. This gives the model a better fit and a better power but beyond certain limits, the validity of the results decreases. Hence, 'PC', the number of significant principal components must be carefully determined so that all information is extracted from the data but no spurious components are included in the model (Eriksson *et al*. 1999, Wold 1978, Wold *et al*. 1984b).

Several methods are available for the determination of 'PC', however cross validation (Eriksson *et al*. 1999, Wold 1978, Wold *et al*. 1984b) which was first suggested by Mosteller and Wallace (Wold 1978) then recently been explored mainly by Stone, Geisser and Allen (Wold 1978) thereafter by Wold, 1978, proved to be one of the most effective methods.

In cross validation, a few of the data elements are kept out from the data matrix each round, and the PC model is fitted to the remaining data (Eriksson *et al*. 1999, Wold 1978). This procedure is repeated until each data element is kept out once and only once. The values of the kept out elements are calculated from the resulting models with different PC and the deviations between calculated and predicted values are evaluated. When the squares of these deviations from the separate "rounds" are summed up, a Predictive Sum of Squares, PRESS, is obtained for each PC. The PC value corresponding to the minimum PRESS is chosen to be used in the model (Geladi *et al*. 1989).

$$PRESS = \sum_{i=1}^{n}\sum_{k=1}^{p}\left(X_{ik} - \hat{X}_{ik}\right)^2 \quad \text{For X matrix}$$

$$PRESS = \sum_{i=1}^{n}\sum_{m=1}^{p}\left(Y_{im} - \hat{Y}_{im}\right)^2 \quad \text{For Y matrix}$$

For every dimension the overall $\frac{PRESS}{RSS}$ is computed, where RSS is the residual sum of squares of the previous dimension. A component is considered significant if $\frac{PRESS}{RSS}$ is statistically smaller than 1.

The evaluation of the performance of a PC model is made by simultaneously considering the explained variation, R2 (goodness of fit) and the predicted variation Q2 (goodness of prediction).

$$R2 = 1 - \frac{RSS}{SS}$$

$$Q2 = 1 - \frac{PRESS}{SS}$$

where, SS is the total variation in data matrix after mean centering. R2 and Q2 are expected to be close to 1 for a significant principal component (Eriksson *et al*. 1999, Geladi *et al*. 1999, Massart *et al*. 1997).

Pesticides are released into the environment through human activities. Once in the environment, pesticides may have many different fates. Volatile pesticides can move through the air and end up in other parts of the environment, such as in soil or water. Pesticides dumped or directly applied to the soil may be transported by surface water runoff into nearby bodies of surface water or may percolate through the soil to lower soil layers and groundwater (De Leeuw *et al*. 2000). The dispersion of pesticides in the environment depends on their properties, that is, most volatile pesticides go into the atmosphere, persistent ones move long distances, whereas pesticides soluble in water are easily carried off with rainwater as runoff or by leaching. Apart from the properties of pesticides, the soil characteristics, that is, soil type, organic matter, metal content, and acidity of the soil also affect the dispersion of pesticides in the environment. Similarly, surface waters vary in their properties such as acidity, depth, temperature, clarity (suspended soil particles or biological organisms), flow rate, and general chemistry and all these affect pesticide movement and fate (McEwen and Stephenson 1979). Pesticide degradation involves the reactions that change most pesticide residues in the environment to inactive and generally less toxic and harmless compounds. These reactions are usually beneficial to the environment (Brown and Hock 1990).

Dechlorination of chlorinated pesticides, that is, the cleavage of C–Cl bond, is a highly important step in the degradation of these xenobiotic substances. Although the C-Cl bond is not absolutely foreign to microorganisims, some of the synthetically produced organic chemicals, including pesticides and their metabolites have structures, which are totally unfamiliar to microorganisms. The microorganisms lack enzymes needed for their degradation (Mansour 1993, Mihale 2002). This is why some pesticides, such as DDT, its metabolites and HCH (hexachlorocyclohexane), are very recalcitrant in the environment. This is the main reason for the general low biodegradability of organochlorine compounds and their persistence in the environment (Mansour 1993).

Very little has been reported in the literature on the chemometric analysis of pesticide residues data. Chemometric methods are useful tools in interpreting pesticide residues data and interactions between the measured variables due to the fact that the data contain multiple variables (Flórián *et al*. 1995, Mujunen *et al*. 1996). Eriksson *et al*. 2000, showed that chemicals released to the environment can be modeled and predicted as a function of the chemical properties of the pollutants by chemometric methods. The chemometric study of the 'spatial and temporal hydrochemical changes in groundwater under the contaminating effects of fertilizers and wastewater' conducted in Galacia, North-west Spain, revealed that the spatial distribution of the environmental pollutants is dictated by the prevailing type of contamination (Vidal *et al*. 2000).

This paper, therefore, reports on the analysis of organochlorine pesticides residues data obtained from samples collected from Vikuge farm, Coast Region, Tanzania between 2000 and 2003 by the use of principal components analysis to disclose their spatial patterns and trends in the environment.

MATERIALS AND METHODS

Materials

The study involved the analysis of pesticide residues analytical data sets obtained from water, surface soil and sediment samples from Vikuge farm in Kibaha district, Coast region. The data analysed included those which were obtained from the study conducted by Mihale 2002 who analysed soil samples from the point source while sediments and water samples were from water streams and wells nearest to the point sources. We then extended the data collection by sampling soil, sediment and water samples moving away from the point source to cover a distance of 7 km following the drainage direction while sampling at intervals of 1 km. The data analysed in this study therefore, were collected from the year 2000 to 2003. These data were collected systematically starting from the source (the place where the obsolete pesticides were dumped many years ago) and then moving away to about 7 km north of the source.

Below are the data Tables (Tables 1, 2 and 3) analysed in this study.

Table 1: Pesticide residues data from Vikuge water samples μg/L.

S/N	Sample	α HCH	β - HCH	γ HCH	δ – HCH	pp'- DDE	pp'- DDD	op- DDT	pp'- DDT	γ – CHL
1	TD	0.48	0.82	0.04	0.01	nd	0.5	0.41	10.07	0.001
2	S1	0.02	nd	0.001	0.013	nd	0.04	0.014	0.08	nd
3	S2	0.64	0.04	0.28	0.016	nd	0.04	1.13	4.67	nd
4	S3	0.01	nd	nd	nd	0.01	0.01	nd	nd	nd
5	S4	0.12	0.26	0.01	nd	0.02	0.13	0.8	0.07	0.005
6	G1	0.03	nd	nd	nd	nd	0.02	nd	0.64	nd
7	G2	0.04	0.002	nd	nd	nd	0.16	nd	6.4	0.002
8	G3	0.07	0.1	0.01	nd	0.02	0.03	0.16	0.91	nd
9	G4	0.01	nd	nd	nd	nd	0.01	0.02	0.25	0.001
10	G5	4.7	1.41	0.2	0.042	0.13	1.12	8.19	19.08	nd
11	G6	3.19	2.44	0.2	0.12	0.13	1.09	4.27	nd	nd
12	G7	0.02	nd	nd	nd	nd	0.04	0.03	0.22	0.004

Note; TD = Tap water, S1 to S4 = Water samples collected from the surface (sampling point 1 to 4), G1 to G7 = Water samples collected from the wells (well 1 to 7), nd = not detected.

Table 2: Pesticide residues from Vikuge surface soil samples in mg/kg dry weight

S/N	Sample	α-HCH	β-HCH	γ-HCH	δ-HCH	pp'-DDE	pp'-DDD	op-DDT	pp'-DDT	γ-CHL
1	B	34227.3	4885.1	5053	776.8	306.33	21535	7446.7	29983.5	49.21
2	C	231.1	1765.2	74.88	193.9	695.58	12240.2	6592.8	13764.1	139.5
3	D	2851.9	343.66	153.4	93.33	144.35	4712.99	2012.1	5231.14	nd
4	20 m	1125.01	2426.6	nd	nd	269.52	12086.8	3756.9	16821.2	59.6
5	100 m N	0.00033	nd	0.001	nd	0.0463	0.0288	0.03	0.3247	nd
6	1 km N	nd	nd	nd	nd	0.0011	0.00215	nd	0.00745	nd
7	2 km N	nd	nd	nd	nd	0.0003	0.0004	nd	0.0016	nd
8	3 km N	nd	nd	nd	nd	0.0002	0.0003	nd	0.0008	nd
9	4 km N	nd	nd	nd	nd	nd	nd	nd	nd	nd
10	6 km N	0.0003	nd	nd	nd	0.0002	0.0005	nd	0.0027	nd
11	7 km N	nd	nd	nd	nd	nd	0.0003	nd	0.0004	nd

Note; B = Sample from the point source, C = Sample from the point source, D = Sample from the point source, 20 m sample collected 20 m away from the point source, 100 m N = Sample collected 100 m away from the point source in North direction, similarly to 1 Km N, 2km N, 3 km N, 4 km N, 6 km N and 7 km N, nd = not detected

Table 3: Pesticide residues data from Vikuge Sediment samples in mg/kg dry weight

S/N	Sample	α-HCH	β-HCH	pp'-DDE	pp'-DDD	0p-DDT	pp'-DDT
1	1U	nd	278.87	98.75	417.61	692.51	nd
2	2U	nd	402.38	267.5	1027.08	1684.84	nd
3	3U	33.72	1549.5	675.3	2053.27	4610.27	nd
4	4U	194.95	3832.99	1633	2778	7946.51	nd
5	1d	1383.21	1158.93	1194	5737.33	6351.68	36420.6
6	2d	276.91	1831.1	889	3812.67	7428.55	20652.79
7	3d	841.59	6546.39	1812	11011.08	16680.5	nd
8	4d	196.62	923.03	504.1	2065.87	3347.71	15444.09
9	3 km N	nd	nd	0.0042	0.0122	0.0299	0.2095
10	4 km N	nd	nd	0.0048	0.0191	0.0103	0.2169

Note; 1U to 4U = Samples collected from point 1 to 4 of Uphill from the point source, 1d to 4d = Samples collected from point 1 to 4 of downhill from the point source whereas 3 km N and 4 km N = Samples collected at that distance from the point source in North direction, nd = not detected.

Methods of Analysis

The principal components analysis of the pesticide residues and their metabolites data was performed using *SIMCA*-P (Soft Independent Modeling of Class Analogy) program [Umetri AB, Umea, Sweden] software (Eriksson *et al*. 1999). Before fitting the PC model, the data were scaled to unit variance (autoscaling). The autoscaling of data provides equal weight of each of the variables to the PC model (Farnham *et al*. 2002). After auto-scaling the PC model was fitted to find out patterns, spatial distribution of the residues components, degradation profiles of pesticide residues and their metabolites, concentrations and relationships among the components. The obtained PCs were used to obtain score (t_1 versus t_2) and loading (p_1 versus p_2) plots. The similarity of samples within a class was assessed by the proximity of samples to each other in plots derived from the principal components models. Score and loading plots were then used to simplify the visualization of the data relationships and patterns, as well as for the detection of outliers. Graphs of variables against samples were drawn to show the concentration decrease or increase of some of the pesticide residues in different samples away from the source. Histograms of individual variable modeling, which show the values of *goodness of fit*, R2 and *goodness of prediction*, Q2, were recorded and used to check the relevance of the model. In performing the multivariate data analysis, the data were grouped according to the media i.e. data from water, soil and sediment samples were separately analysed to reveal the behavior of pesticides, metabolites and residues in the respective media.

RESULTS AND DISCUSSION

Data from Water Samples

After scaling to unit variance the PC model was fitted. This resulted into one significant principal component in accordance with the cross validation criterion (Eriksson *et al*. 1999, Wold 1978). Due to the high percentage of the data variance explained by the first principal component alone (i.e 80.3%), it is clear that the distribution and degradation patterns of these nine pesticide residues in water are strongly correlated (Eriksson *et al*. 1999). Fig. 1a and 1b show the overview of the PCA model with two principal components and the overview of the individual variables respectively.

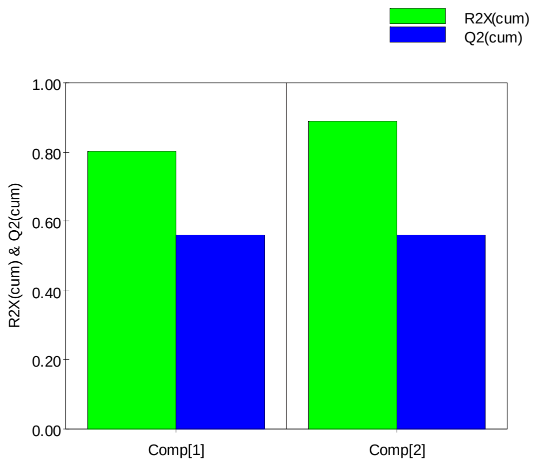

Figure 1a: Overview of the PCA model.

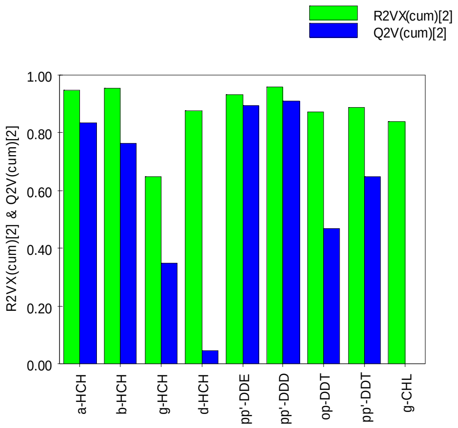

Figure 1b: Overview of the individual variable modeling.

Note; a-, b-, g- and d- on HCH; stands for α-, β-, γ- and δ-, respectively; whereas g- on CHL stands for γ-, Fig. 1b.

Fig. 1b shows the modeling of the individual variables, and shows that α-HCH, β-HCH, γ-HCH, pp'-DDE, pp'-DDD, pp'-DDT and op'-DDT are well modeled while, δ-HCH and γ-chlordane are not well captured by the model. This may be due to the quantities of these residues in the water, i.e the values of δ-HCH and γ-chlordane in the samples were very low or not recorded at all as they were below detection limit. It was observed that all the variables are highly loaded in the first PC except γ-chlordane, which is highly loaded in PC2. This implies that the distribution and degradation profile of these pesticide residues in water samples obtained from Vikuge is highly correlated (Eriksson *et al*. 1999). However, the loading of γ-chlordane in PC2 unlike the other pesticides indicates the existence of dissimilarities in some of the chemical properties governing these compounds in the environment. It has been reported that γ-chlordane binds tightly to soil particles and is not likely to enter into water column, hence its low levels in water samples (Cioce 2008, Wiberg 2001). This explains why only traces were obtained in water samples.

The score and loading plots (Fig. 2a and 2b) were recorded to show the distribution pattern of the pesticide residues and their metabolites in the sampled water. The score plot shows that observations S2, G5 and G6 are lying somewhat far from the rest of the data points but inside the Hotelling's T^2 tolerance ellipse. It can be observed that the rest of the observations form one cluster within the Hotelling's T^2 tolerance ellipse, Fig. 2a. Hotelling's T^2 is the detection tool for strong outliers and is a multivariate generalization of student's t-test. It provides a check for observations adhering to multivariate normality. When used in conjunction with a score plot, Hotelling's T^2 defines the normal operating area corresponding to, for instance, 95% or 99% tolerance (Eriksson *et al*. 1999).

Samples G5 and G6 are among the ground water samples (Mihale 2002). These samples were observed to have the highest concentrations of all the measured pesticide residues in water at the studied site compared to the rest of the samples. Generally, ground water samples showed higher levels of pesticide residues and their metabolites than either tap or surface water samples. The extent of ground water contamination by pesticides is usually determined by the magnitude of the sources, opportunities for interaction through the soil, chemical properties of the pesticides and geological conditions. The interaction between the pollutant and environmental conditions controls the pollutant's behavior and ultimately its effect on the environment (Barbash and Resek 1996). The water samples were collected following the drainage system of Vikuge and therefore the accumulation of pesticide residues observed in ground water samples G5 and G6 was probably due to the sloping nature of the site. Observation S2 (surface water sample) showed relatively high concentrations of pp'-DDT and op-DDT. The loading plot, Fig. 2b, shows two main groups of the pesticide residues variables.

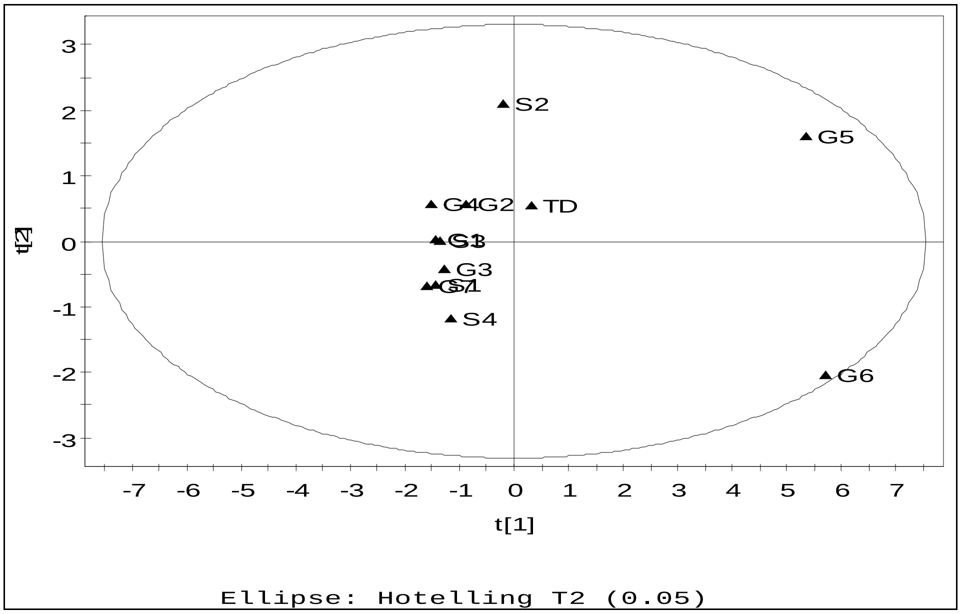

Figure 2a: Score plot of data from water samples. Data point labels as defined on Table 1.

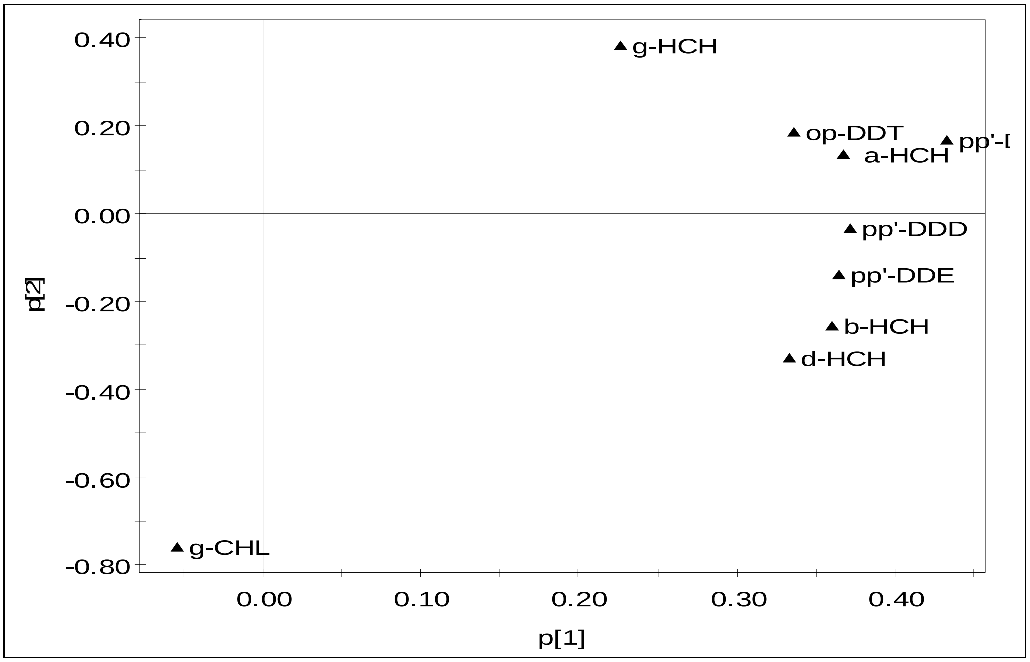

Figure 2b: Loading plot for data from water samples; Note; a-, b-, g- and d- on HCH; stands for α-, β-, γ- and δ-, respectively; whereas g- on CHL stands for γ-.

One group consists of α-HCH, op'-DDT and pp'-DDT, whilst the second group is comprised of β-HCH, δ-HCH, pp'-DDE and pp'-DDD. γ-HCH is somewhat far from these clusters. γ-chlordane, on the other hand, is positioned at the opposite side of the rest of the variables and is highly loaded into PC2. These pesticide residues in water samples (except γ-chlordane), therefore, indicate that they undergo degradation since they are clustered at the right hand side of the loading plot (Eriksson *et al*. 1999). The position of γ-chlordane in the loading plot, i.e. very far from the main cluster and at the opposite direction to the rest of the variables, means that, it is negatively correlated to the rest of the variables.

A line plot (Fig. 3) for these data was recorded in order to study the variation of the concentrations of the pesticide residues and their metabolites in water with increasing distance from the point source and also their distribution trend in tap water (TD), surface water (S1 – S4) and well water (G1 – G7). The plot shows that, generally there is no clear trend of pesticide residues and their metabolites concentration with increasing distance from the source. Sample number 7 (G2, sample collected from well 2) has shown high concentration of pp'-DDT, while sample number 10 (G5) has shown to have high concentrations of pp'-DDT, α-HCH and op'-DDT in the order; pp'-DDT > op'-DDT > α-HCH, with relatively increasing distance from the points nearest to the source. Pesticide residues are carried by volatilization and runoff water away from the source and deposited in the water and sediments. This makes the sediments to be a secondary contamination source by continuously releasing the residues in the aqueous media through sediment-water interface equilibration. Also, due to the sandy nature of Vikuge soil (Mihale 2002), leaching of pesticide residues to the groundwater (wells) is favored. The concentration of the DDTs in groundwater samples (wells) is higher than that of HCHs. This may be due to the rapid mineralization and formation of volatile organic compounds by the HCHs. This observation is similar to results obtained in a study done in India (Singh 2001). In the study of the comparison of organochlorine pesticide levels in soil and groundwater of Agra, India, conducted by Singh, it was observed that the concentration of DDTs was higher compared to those of HCHs, contrary to expectation. Due to higher solubility of HCHs, their concentrations were expected to be much higher than DDTs in groundwater (Singh 2001). The rest of the samples have shown a decreasing trend of the pesticide residues with increasing distance from the source. A similar trend of decreasing DDT and HCH levels has been reported in a study in the Baltic sea by Roots and Zitko (Roots and Zitko 2003). It was reported that the organochlorine pesticides and PCB concentrations were higher near Riga city, the only local pollution source in the Baltic countries, but decreased in a gradient to background values at Saaremaa, which is away from the city. The results showed that there was a fast decrease of the pollutant load with increasing distance from the supposed source area. A decreasing trend with increasing distance from pollution source has also been reported in a study conducted in the Norwegian and Russian Arctic by Lie *et al* (Lie *et al*. 2003). It was found that HCHs levels closer to the possible pollution sources along the coast of Russia were higher than the open parts of the East Arctic ocean. Thus, concentrations of organochlorine pesticides were lower in the samples from regions far away from the pollution source (Lie *et al*. 2003).

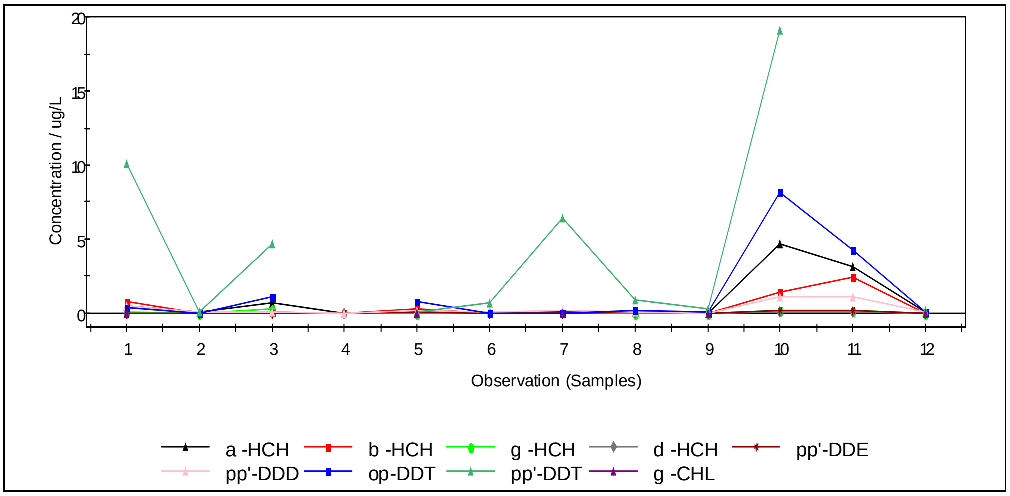

Figure 3: Line plot showing the distribution and variation of pesticide residues concentration in different water sampling points in relation to the distance from the source. Note; a-, b-, g- and d- on HCH; stands for α-, β-, γ- and δ-, respectively; whereas g- on CHL stands for γ-. Numbers on the x-axis corresponds to the sampling points on Table 1.

Data from Surface Soil Samples

The data collected from surface soil samples were first scaled to unit variance (auto scaling). The PCA model fitted to the data resulted into two significant principal components according to the cross validation criterion (Eriksson *et al*. 1999, Wold 1978). The obtained PCs explained 97.6% of the total variation of the data (R2 = 0.976 and Q2 = 0.745) (see model overview, Fig. 4a).

The first principal component explains 78.6% of the total variance of the data, and this implies that the degradation patterns of the pesticide residues in the surface soil environment are highly correlated. Thus, the rate of degradation and microbial activities for all the pesticide residues in the surface soil are similar.

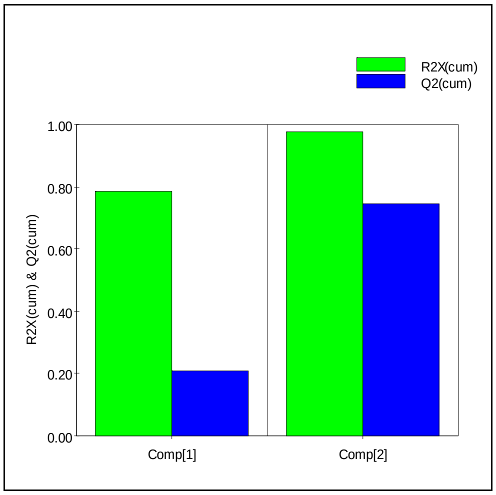

Figure 4a: Model overview for data from surface soil samples

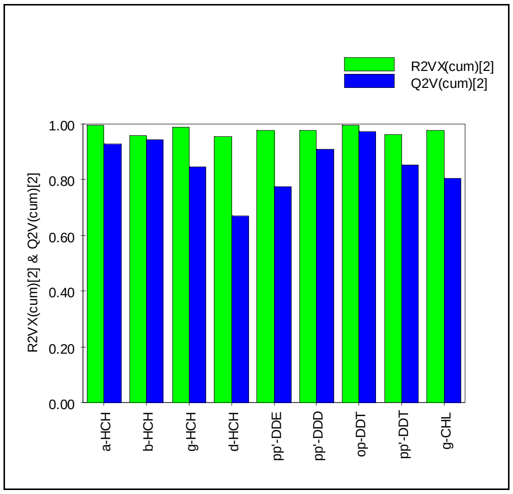

Figure 4b: Model overview of individual variables

Note; a-, b-, g- and d- on HCH; stands for α-, β-, γ- and δ-, respectively; whereas g- on CHL stands for γ-, Fig. 4b.

Fig. 4b shows the modeling of each variable. It is observed that all the variables are well modeled since the values of R2 and Q2 for each variable match well (Eriksson *et al.* 1999).

The score plot (Fig. 5a) shows the data to be clustered at the origin with observations B identified as a strong outlier since it lies outside the Hotelling's T^2 tolerance ellipse. Observation B contain data from sample collected from the point source and it was found to contain very high concentrations of all the measured pesticide residues compared to the rest of the samples. The loading plot (Fig. 5b) shows three main groups of the variables. All the variables are located at the right hand side of the loading plot, indicating that they all undergo similar distribution and degradation patterns. The clustered variables have similar chemical behavior in this environment.

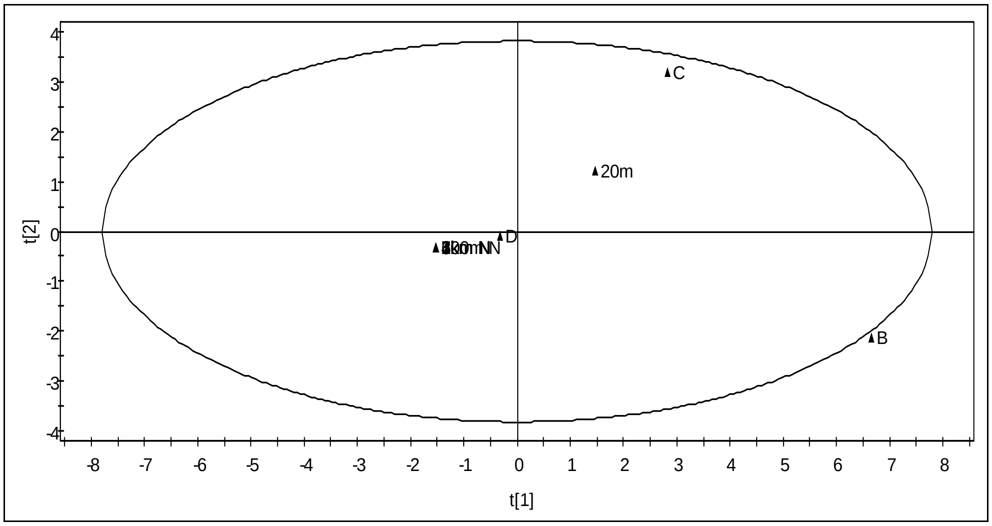

Figure 5a: Score plot for data from surface soil samples; data points labels as defined on Table 2.

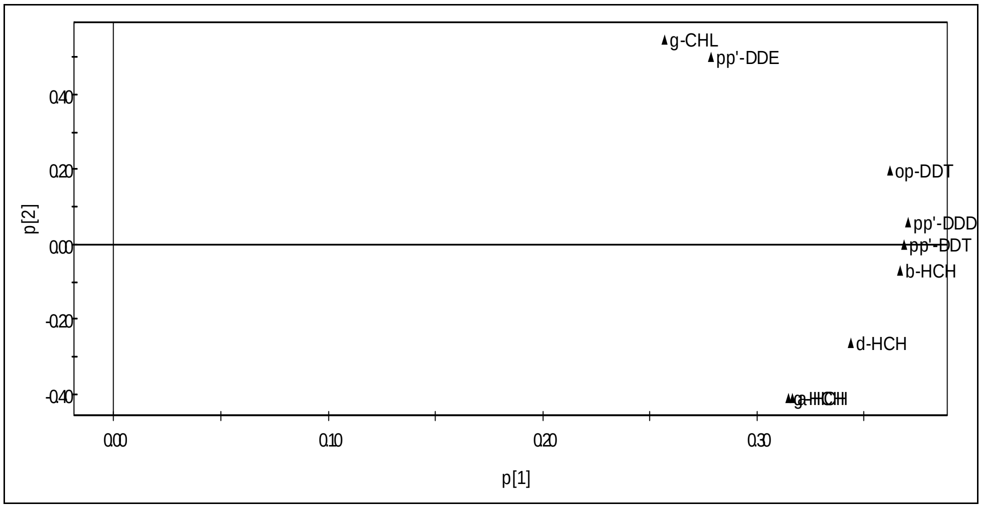

Figure 5b: Loading plot for data from surface soil samples. Note; a-, b-, g- and d- on HCH; stands for α-, β-, γ- and δ-, respectively; whereas g- on CHL stands for γ-

Fig. 6 shows the trend of the variation of the concentrations of the pesticide residues and their metabolites in the surface soil. The plot shows that the concentrations of the pesticide residues and their metabolites generally decrease with increasing distance from the source. A similar trend has also been reported by Mihale (Mihale 2002), Roots *et al* (Roots and Zitko 2003) and Lie *et al* (Lie *et al*. 2003).

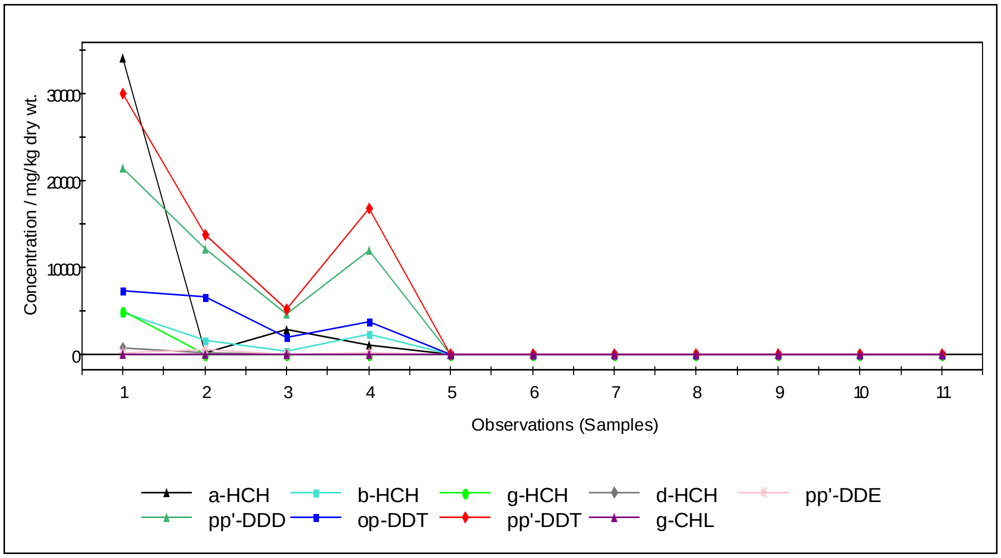

Figure 6: Variation of pesticide residues concentration with increasing distance from the source. Note; a-, b-, g- and d- on HCH; stands for α-, β-, γ- and δ-, respectively; whereas g- on CHL stands for γ-. Numbers on the x-axis corresponds to the sampling points on Table 2.

Data from Sediment Samples

The PC model was fitted to the scaled data and resulted into two significant principal components. The obtained principal components explained 95.7% of the total variance of the data. The PC model captured well all the variables analysed as shown in Fig. 7a and 7b.

All the variables were highly loaded into the first principal component except α-HCH, which was highly loaded into the second principal component

In the score plot (Fig. 8a) one group of the data, which is clustered around the origin is observed, while observations 1d and 3d are away from this main cluster, but within the Hotelling's T^2 tolerance ellipse. It is interesting to note that α-HCH is located away from the rest of the variables in the loading plot (Fig. 8b). α-HCH has been observed to exhibit different characteristics in these samples and sample 1d contains very high concentration of α-HCH. Sample 1d, is a sample collected down the hill along the drainage of Vikuge, and therefore accumulation of pesticide residues at this sampling site was expected.

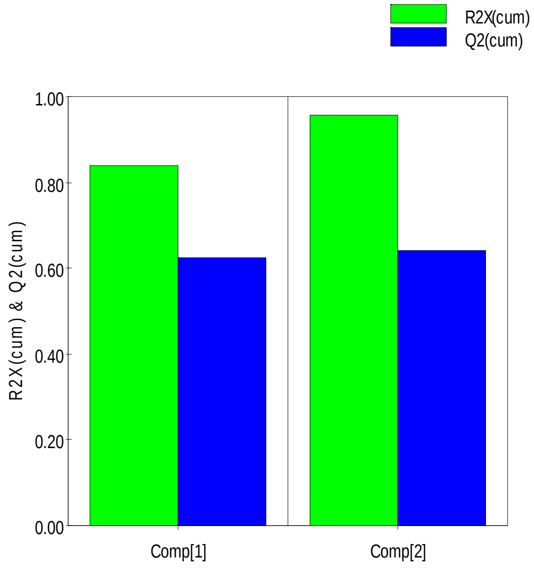

Figure 7a: Model overview for sediment samples.

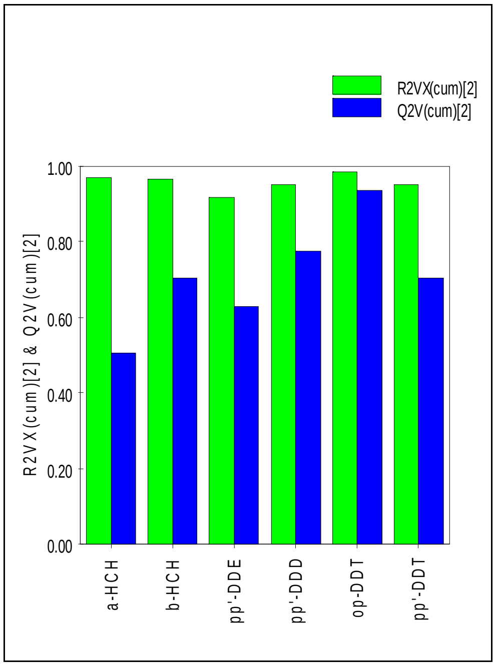

Figure 7b: Modeling of individual variables for sediment samples.

Note; a- and b- on HCH; stands for α- and β-, respectively, Fig. 7b.

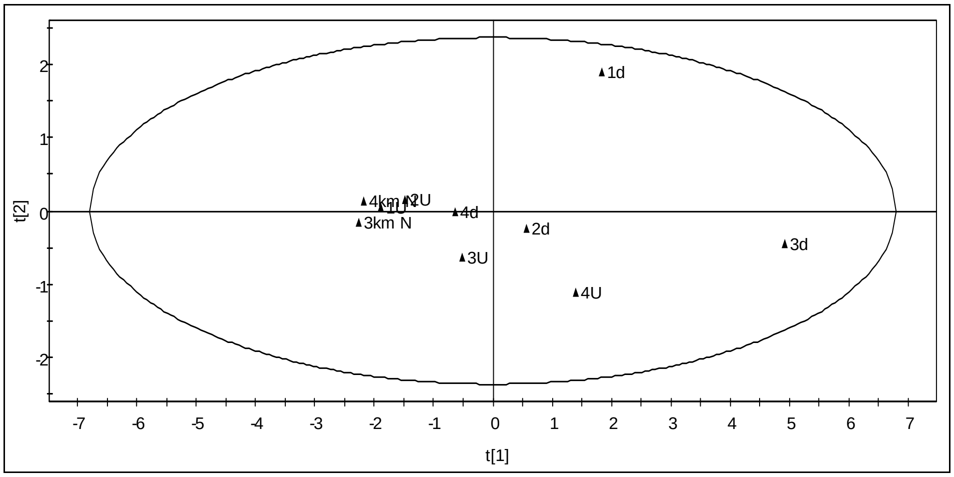

Figure 8a: Score plot for the data from sediment samples. Data point labels as defined on Table 3

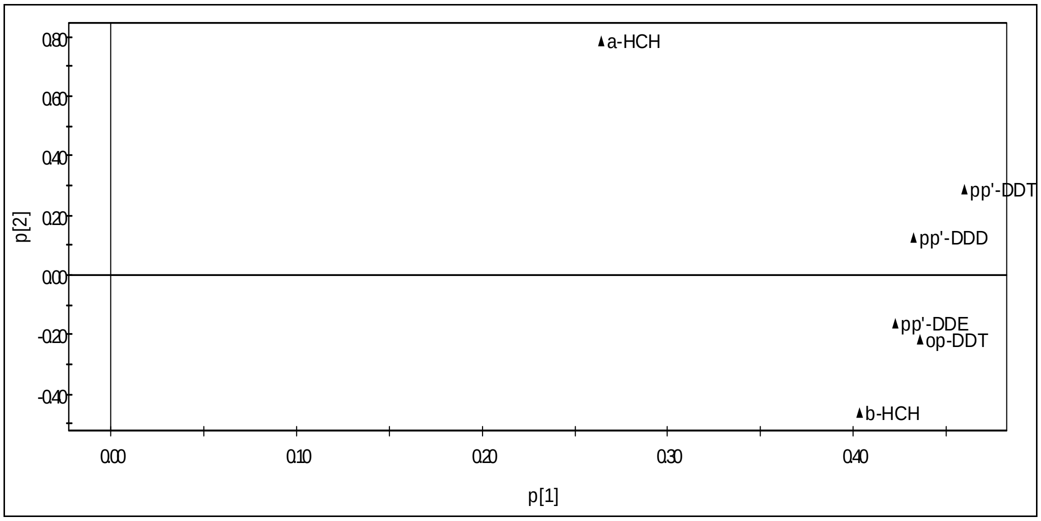

Figure 8b: Loading plot for the data from sediment samples. Note; a- and b- on HCH; stands for α- and β-, respectively.

The loading plot also shows that five variables form a cluster on the first PC, verifying their similar behavior in the sediments. The line plot, Fig. 9, shows that there is an increase in the concentration of the pesticide residues with increasing distance from nearest point to the point source. This trend was not expected. However, it can be explained by the fact that the sediment samples were collected from the hill going downwards following the drainage of Vikuge. For example, observation number 7 (sample 3d) revealed a very high concentration of op-DDT, pp’-DDD and β-HCH away from the source.

This observation contained samples from down the hill, and pesticides washed from up hills are expected to accumulate at this location. Hence, an overall increase in concentrations of pesticide residues was recorded (Mihale 2002) along the ditch from uphill to downhill. This can be explained by the flowing water’s ability to carry the residues either in solution or in suspension downhill. Mihale, 2002 reported a similar trend of pesticide residues in sediments. This observation is also supported by a report by Aguilar *et al* (Aguilar *et al*. 2002), in a study of the geographical and temporal variation in levels of organochlorine contaminants in marine mammals. It was observed that organochlorine contaminant concentrations tended to decrease in the regions where pollution was initially high but increased in regions located far from the pollution source as a consequence of atmospheric transport and redistribution (Aguilar *et al*. 2002).

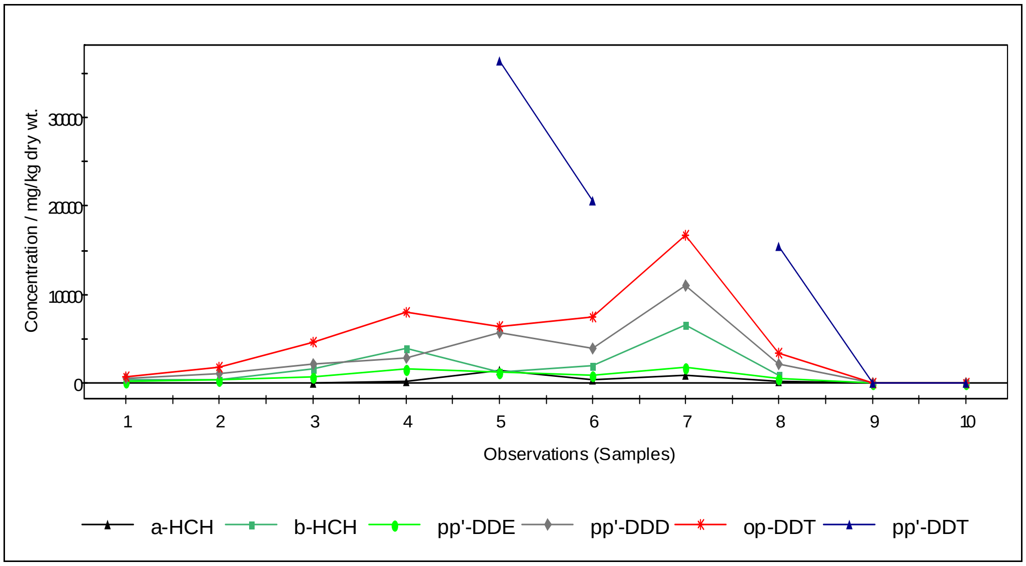

Figure 9: Line plot showing the variation of pesticide residues concentration in sediments samples. Note; a- and b- on HCH; stands for α- and β-, respectively. Numbers on the x-axis corresponds to the sampling points on Table 3.

CONCLUSIONS AND RECOMMENDATIONS

Principal Components Analysis of the water, soil and sediment data sets from Vikuge has revealed that the obsolete pesticides dumped at Vikuge pasture farm undergo degradation with time. It was also found that the concentration of pesticide residues in the Vikuge environment decreases with increasing distance from the area where the obsolete pesticides were dumped (point source). However, analysis of the data from sediment samples has shown an increase in concentration with increase in distance from the nearest point to the point source. The surface soil samples were found to be mostly contaminated while water showed to be the least contaminated, with the trend being: surface soil > sediments > water.

Based on the findings of this study it is recommended that:

1. Control measures should be taken to avoid further contamination of the areas around Vikuge farm.
2. Users of the pesticides and the community should be educated on the proper handling of these chemicals to avoid their side effects.

ACKNOWLEDGEMENTS

We are pleased to acknowledge Mr. Matobola Mihale who allowed us to include the data from his MSc work. We also extend our acknowledgement to Dr. John A. M. Mahugija whom we collected the rest of the samples together to cover a distance of 7 km from the point source. Further thanks are due to Sida/SAREC for funding this study through the Directorate of Postgraduate Studies of the University of Dar es Salaam.

REFERENCES

Aguilar A, Borrell A, Reijnders PJH 2002 Geographical and temporal variation in levels of organochlorine contaminants in marine mammals. *Marine Environmental Research*. 53: 425-452.

Barbash J and Resek EA 1996 Pesticides in groundwater; distribution, trends and governing factors. Lewis Publishers, New York, USA.

Brown CL and Hock WK 1990 The fate of pesticides in the environment. Agrochemical Fact sheet No 8. Penn state cooperative extension.

Ciose D 2008 The patterns of Distribution of Organochlorine Pesticides in Sediment in the Letort Spring Run, Cumberland Country, Pennsylvania, Department of Environmental Studies, Dickinson College. www.dickinson.edu/uploadedFiles/academics/programs/environmental-studies/content/Cioce%201R08.pdf. Accessed on 26 November 2012.

De Leeuw FAAM, Van Pul WAJ, Berg FVD and Gilbert AJ 2000 The Use of Atmospheric Dispersion models In Risk Assessment Decision Support Systems for Pesticides. *Environmental Monitoring and Assessment*, **62**: 133-145.

Eriksson L, Johansson E, Muller M and Wold S 2000 On the selection of the training set in environmental QSAR analysis when compounds are clustered. *J. Chemometrics*, **14**: 599-616.

Eriksson L, Johansson E, Kettaneh-Wold N and Wold S 1999 Introduction to Multi– and Megavariate Data Analysis Using Projection Methods (PCA & PLS) Umetri AB, Umea, Sweden.

Farnham MI, Singh KA, Stetzenbach JK and Johannesson HK 2002 Treatment of nondetects in multivariate analysis of groundwater geochemistry data. *Chemom. Intell. Lab. Syst.*, **60**: 265-281.

Flórián K, Matherny M and Pliešovska N 1995 Spectrochemical Methods in Environmental Analysis: Methodology and Chemometrical Investigations. *Microchem. J*. 51: 26-38.

Geladi P, Isaksson H, Lindqvist L, Wold S and Esbensen K 1989 Principal component analysis of multivariate images. *Chemom. Intell. Lab. Syst.* **5**: 209-220.

Geladi P, Hadjiiski L and Hopke P 1999 Multiple Regression for Environmental Data: Nonlinearities and Prediction Bias. *Chemom. Intell. Lab. Syst*. 47: 165-173.

Lie E, Bernhoft A, Riget F, Belikov SE, Boltunov AN, Derocger AE, Garner GW, Wiig O and Skaare JU 2003 Geographical distribution of organochlorine pesticides (OCPs) in polar bears (Ursus maritimus) in the Norwegian and Russian Arctic. *The Science of the Total Environment.* **306**: 159-170.

Massart DL, Vandeginste BGM, Buydens LMC, De Jong S, Lewi PJ and Smeyers-verbeke J 1997 Handbook of Chemometrics and Qualimetrics, Part A, Elsevier Science B. V., Amsterdam.

Mansour M 1993 Fate and prediction of environmental chemicals in soil, plants and aquatic systems. Boca Raton, Florida, USA, Lewis Publishers. 291p.

McEwen FL and Stephenson GR 1979 The Use and Significance of Pesticides in the Environment. A Wiley Interscience Publication, New York.

Mihale MJ 2002 Chemodynamics of Obsolete Pesticides at Vikuge Farm, Kibaha District, Tanzania, *M. Sc. Thesis*, University of Dar es Salaam, Tanzania.

Mujunen S, Minkkinen P, Holmbom B and Oikari A 1996 PCA and PLS methods applied to ecotoxicological data: Ecobalance project. *J. Chemometrics*, **10**: 411-424.

Roots O and Zitko V 2003 Chlorinated Environmental Contaminants (PCB, DDT, HCH and PCDD / PCDF) from the Baltic Sea. Chemistry Preprint Server. CPS: envichem/0308001.

Singh RP 2001 Comparison of Organochlorine Pesticide Levels in Soil and Groundwater of Agra, India. *Bull. Environ. Contam. Toxicol.* **67**: 126-132.

Vidal M, Melgar J, Lopez A and Santoalla MC 2000 Spatial and temporal hydrochemical changes in ground water under the contaminating effects of fertilizers and wastewater. *Journal of Environmental Management,* **60**: 215-225.

Wiberg K 2001 Enantiospecific analysis and environmental behavior of chiral persistent organic pollutants (POPs), *PhD. Thesis*, Umea University, Umea, Sweeden.

Wold S 1978 Cross-validatory estimation of the number of components in factor and principal components models. *Technometrics.* **20**: 397-405.

Wold S, Albano C, Dunn WJ, Edhund U, Esbensen K, Geladi P, Hellberg S, Johanson E, Lindberg W and Sjöström M 1984a Multivariate data analysis in chemistry. In B.R. Kowalski (ed.), *Chemometrics, Mathematics and Statistics in Chemistry*. D. Reidel Publishing Company, 17 - 95p.

Wold S, Albano C, Dunn WJ, Esbensen K, Hellberg S, Johansson E, Lindberg W and Sjöström M 1984b Modelling data tables by principal components and PLS: class patterns and quantitative predictive relations. *Analusis*. **12**: 477-485.