DETECTION AND DISCRIMINATION OF ORGANOPHOSPHORUS PESTICIDES IN WATER BY USING A COLORIMETRIC PROBE ARRAY

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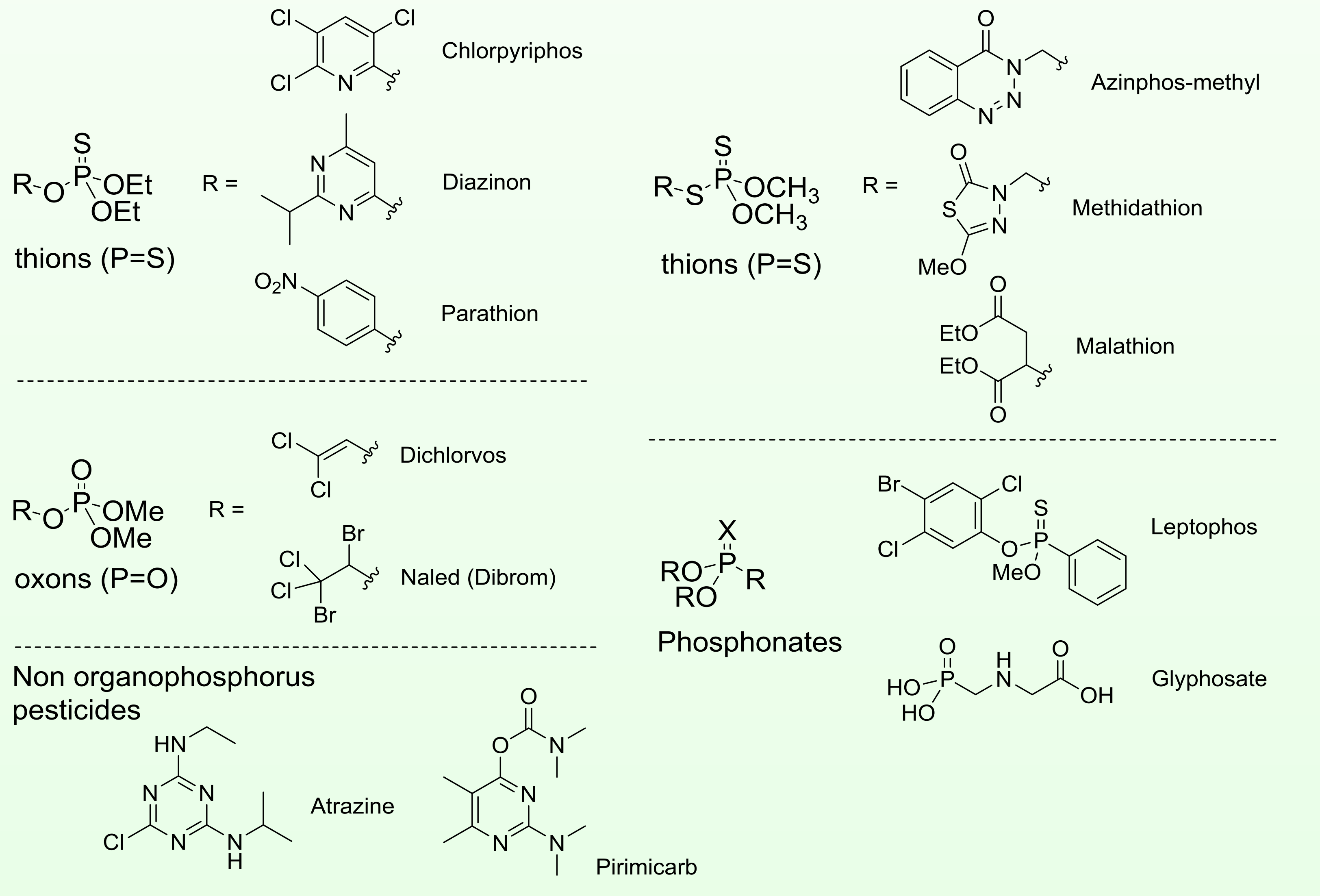
Organophosphorus pesticides (OPs) constitute nowadays the most widely used class of available pesticides. OPs are not only highly toxic to insects but also to human beings. In fact they are one of the most common causes of poisoning of humans across the world via intoxication through inhalation, ingestion or skin absorption[1].

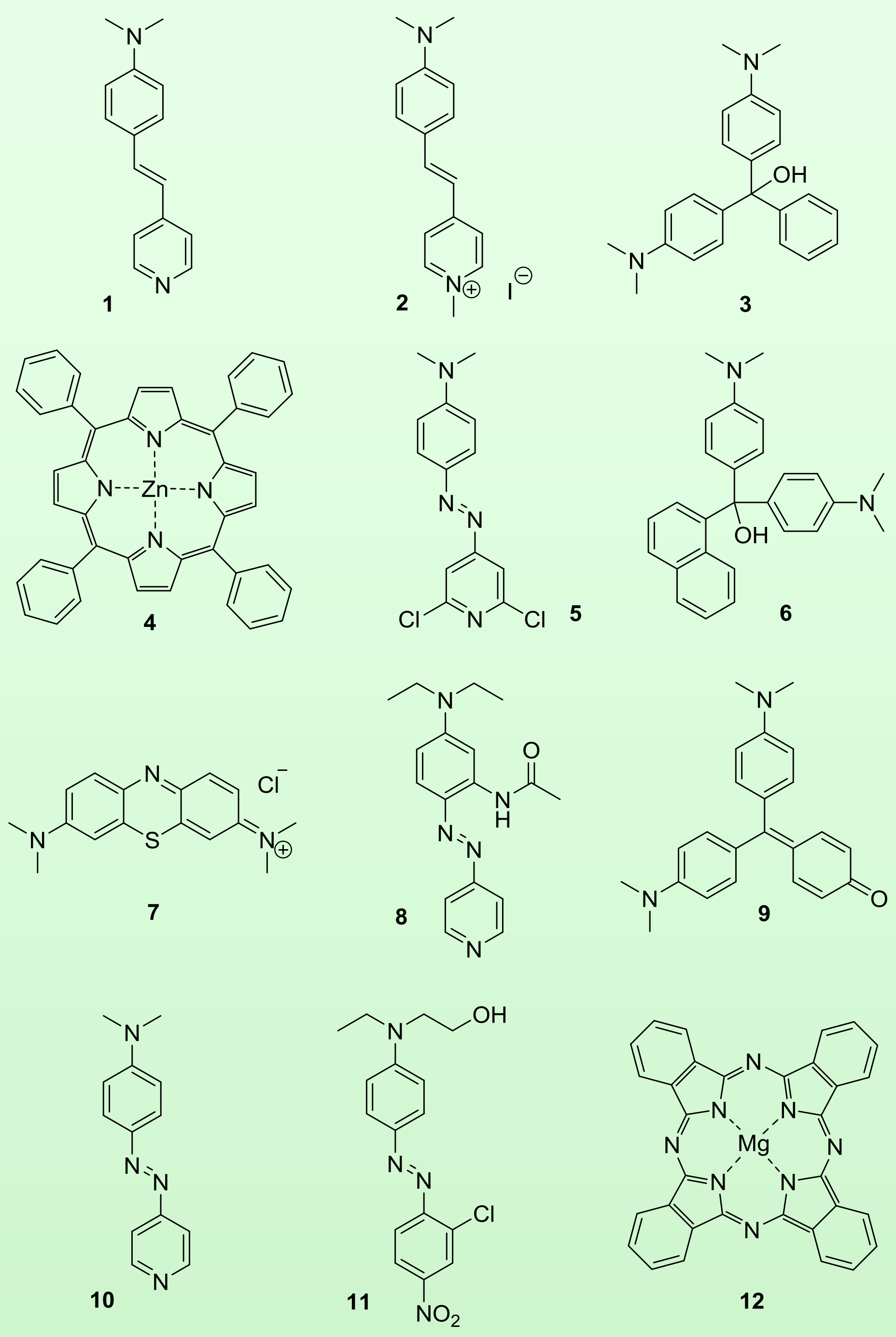
Optical sensing of OPs using chromogenic probes is particularly appealing because colour modulations can be measured using low-cost systems, or in some cases they can be easily detected by the naked eye. In this field, the design of array-based systems (also known as optoelectronic noses) is becoming increasingly popular due to their capability of multianalyte sensing and versatility and the possibility to be applied in complex systems[2].

Chemically, OPs can be classified in three main groups, namely organophosphates, which contain a P=O bond (oxon pesticides), organothiophosphates, in which the oxygen has been replaced by a sulfur atom, (P=S, thions), and organophosphonates which are closely related to nerve agents such as Sarin, Soman or Tabun.



Scheme 1. Chemical structures of the ten organophosphorus and two non-organophosphorus pesticides used in this study.

Inspired by our own experience in the field[3], a 12-member colorimetric array, based in the use of push-pull chromophores containing reactive sites, has been prepared and used for the detection or classification of different pesticides in water. A clear classification was observed for Malathion, Leptophos, Dichlorvos, Dibrom and Diazinon[4].



Scheme 2. The 12 dyes used in the chromogenic array.

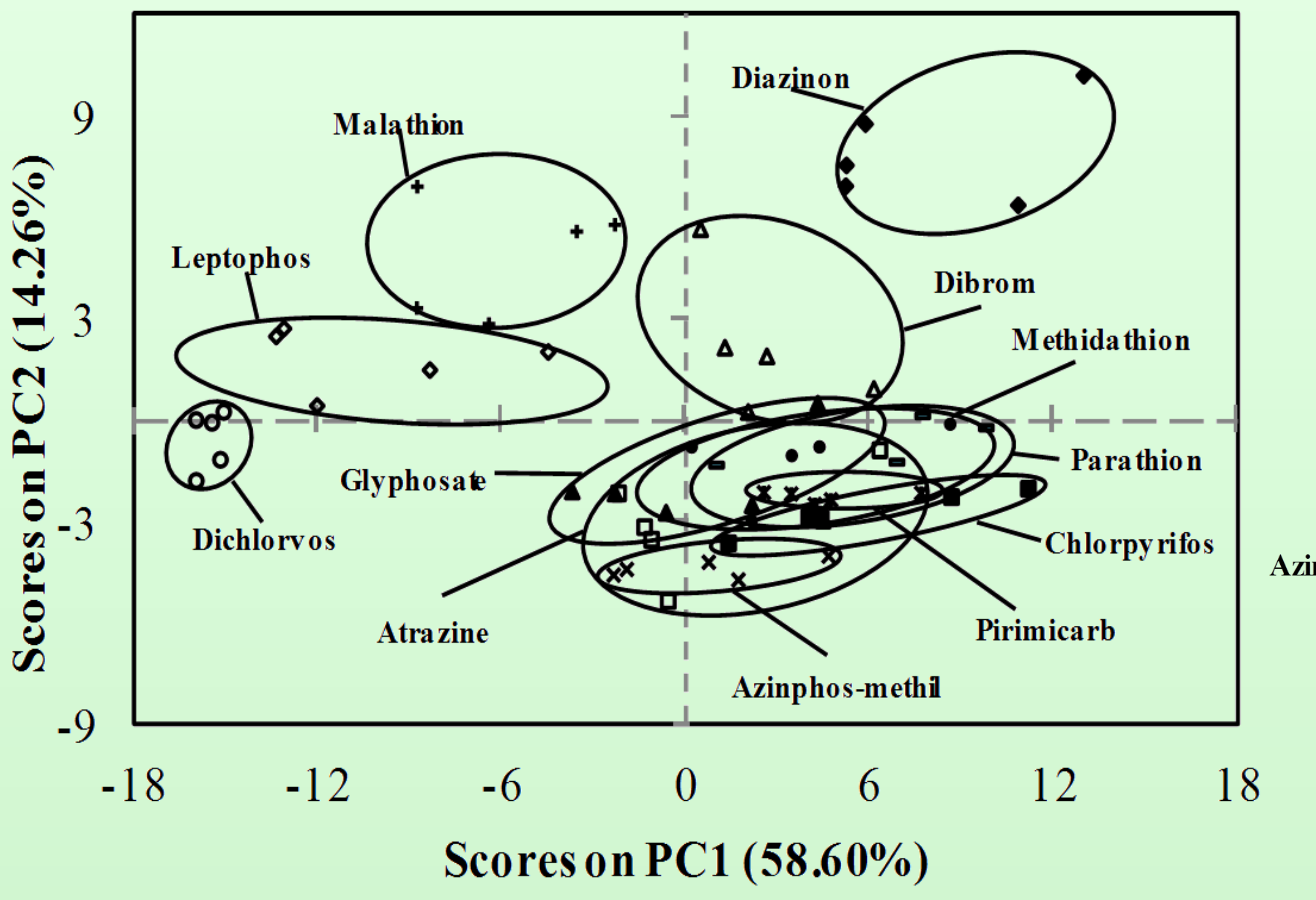


Fig. 1. PCA score plot of PC1 and PC2 for pesticides in Scheme 1 (5 each) and the trial clustering.

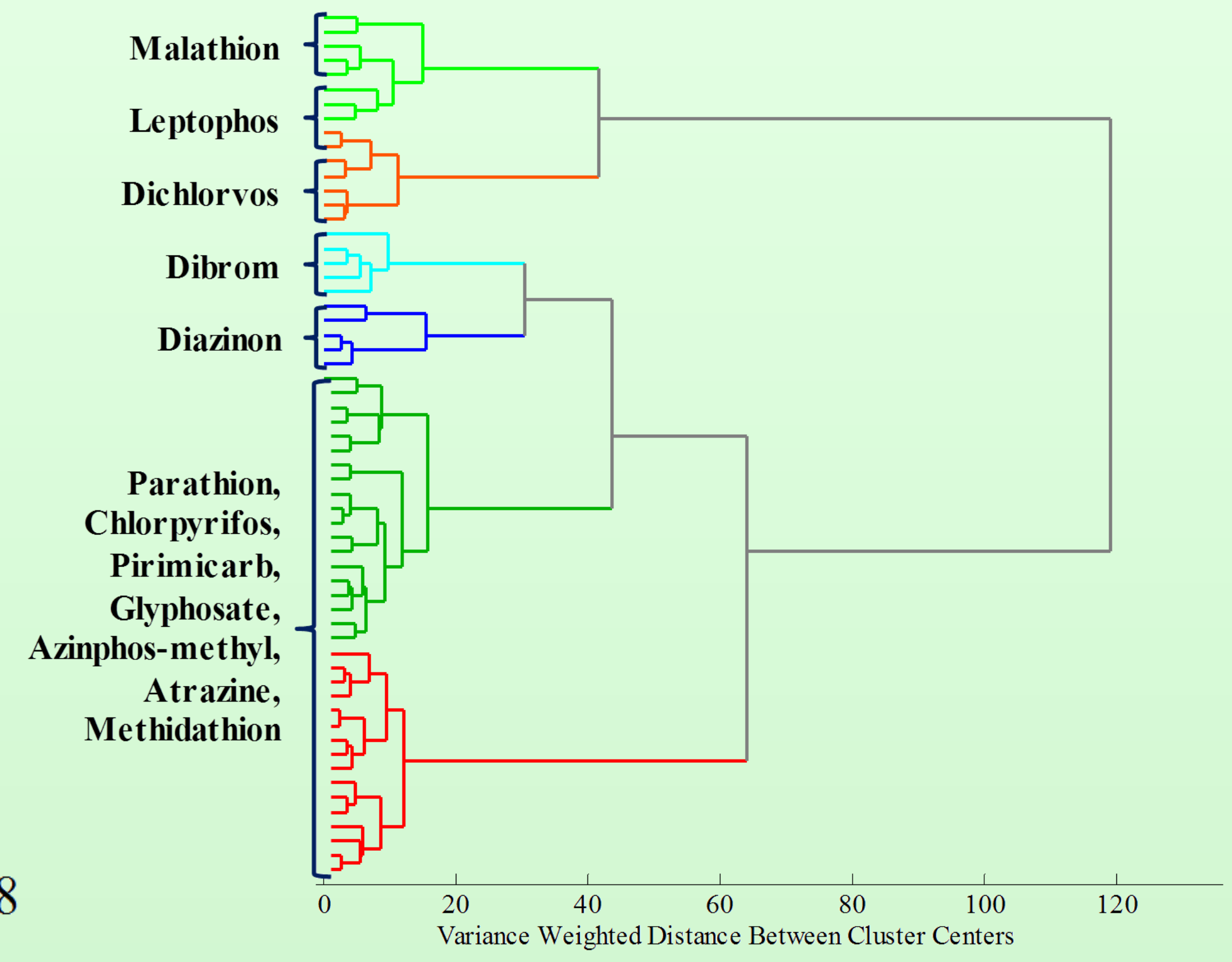
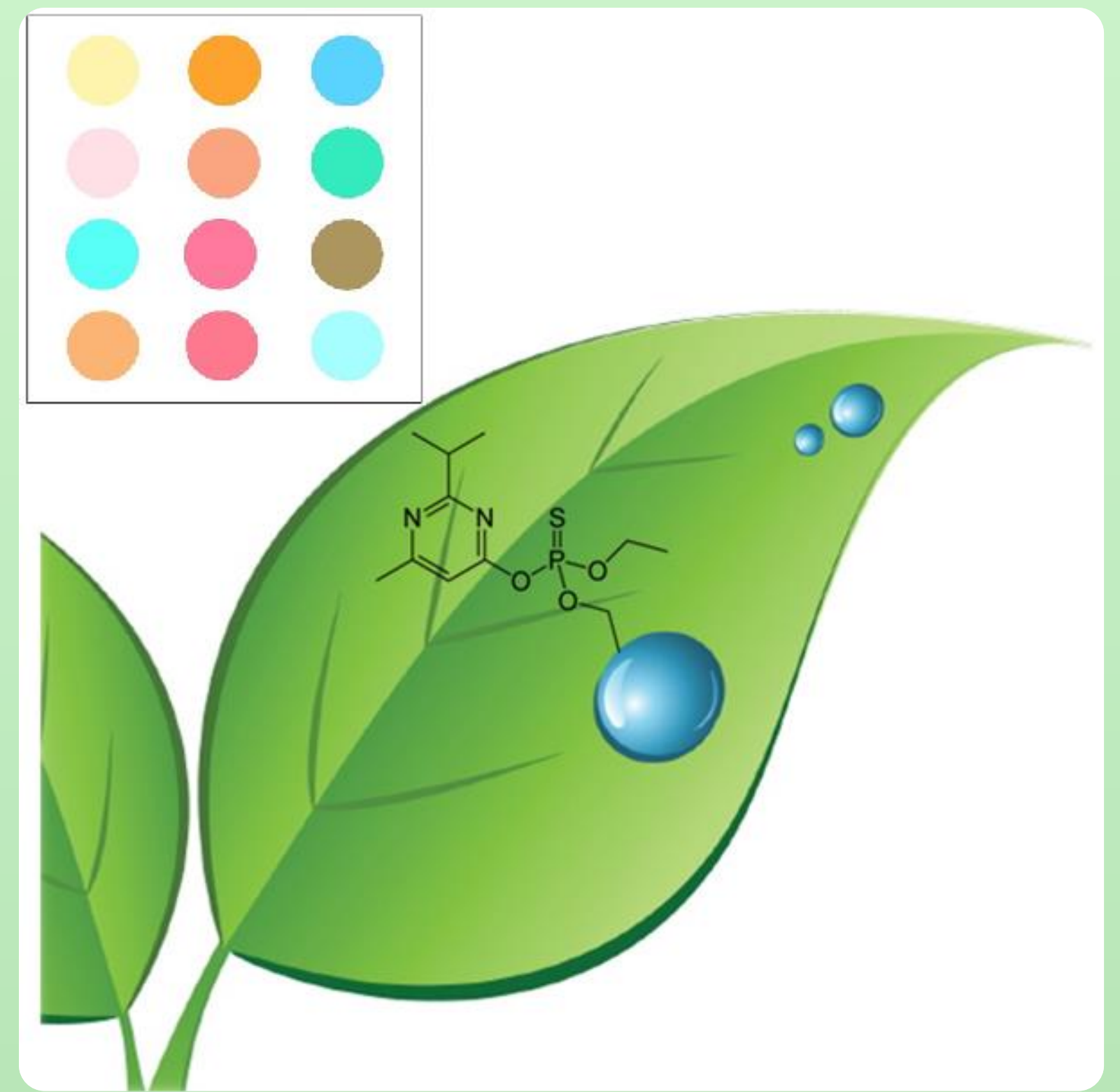


Fig. 2. HCA dendrogram showing the Euclidean distances between the trials.



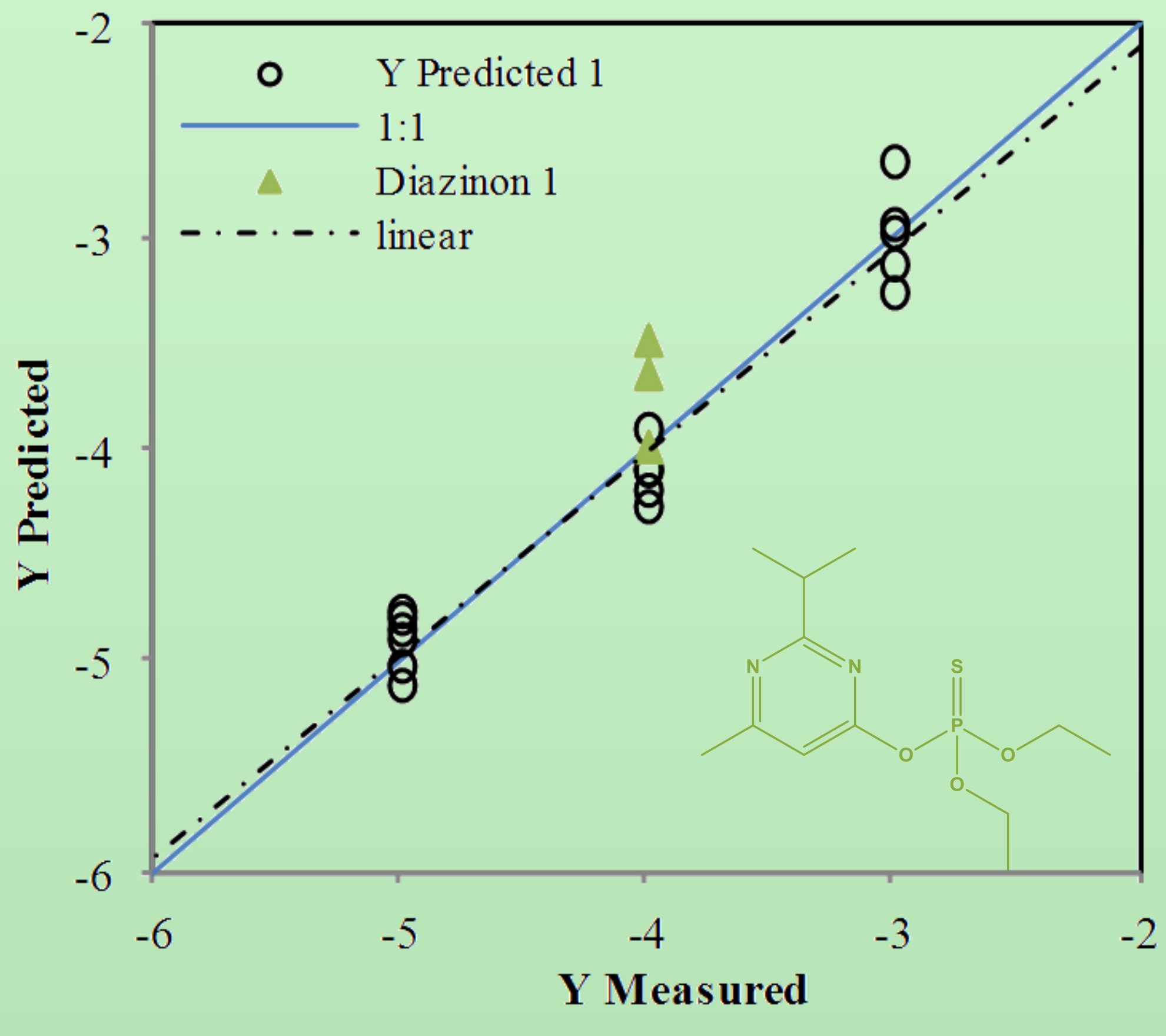


Fig. 3. Plot score of prediction model of Diazinon for samples prepared with both the calibration set (o) and in orange leaves (validation set), (Δ).

Moreover the chromogenic array was able to detect and predict concentration levels of Diazinon in leaves from orange trees in the concentration range of 10^{-3} M to 10^{-5} M.

References
[1] B. Walker Jr, J. Nidiry, Inhal. Toxicol. **2002**, 14, 975-990.
[2] J. R. Askim, M. Mahmoudi, K. S. Suslick, Chem. Soc. Rev. **2013**, 42, 8649-8682.
[3] K. Chulvi, P. Gaviña, A. M. Costero, S. Gil, M. Parra, R. Gotor, S. Royo, R. Martínez-Máñez, F. Sancenon, J. L. Vivancos, Chem.Commun. **2012**, 48, 10105-10107.
[4] D. Ferri, P. Gaviña, A. M. Costero, M. Parra, J. L. Vivancos, R. Martínez-Máñez., *Sensors and Actuators B*, **2014**, *202*, 727–731.