HYDROPHOBICITY OF CHEMICAL COMPOUNDS INCLUDING PESTICIDES IN THE ENVIRONMENT

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Hydrophobicity is an important property of chemical compounds. The logarithm of the partition coefficient in 1-octanol/water (log P or log P_{ow}) is commonly used as an index of hydrophobicity. The highly hydrophobic chemical compounds which have large log P values may accumulate in the environment, causing general toxicity for wild organisms.

In this paper, the relationships of aquatic toxicity and bioconcentration with log P and another hydrophobicity index, the logarithm of the membrane accumulation index, log P_M were explained. In addition, the brief results of our research on pesticide accumulation in Vietnam were described.

Key Words : hydrophobicity, log P, log P_{M}, aquatic toxicity, Bioconcentration Factor, pesticide accumulation, shellfish, Vietnam

1. INTRODUCTION

Hydrophobicity is an important property of chemical compounds. The logarithm of the partition coefficient in 1-octanol/water (log P or log P_{ow}) is commonly used as an index of hydrophobicity. The P values are experimentally determined by the Shake-Flask method (OECD Test Guideline 107) or High Performance Liquid Chromatography (HPLC) Method (OECD Test Guideline 117)\(^1\). The highly hydrophobic chemical compounds which have large log P values may accumulate in the environment, causing general toxicity for wild organisms. The aquatic toxicity of simple compounds has long been recognized as being closely related to their hydrophobicity\(^2\). In this paper, the relationships of aquatic toxicity or bioconcentration with log P were explained. Another hydrophobicity index, the logarithm of the membrane accumulation index, log P_M was also proposed and used for the relationships instead of log P. In addition, the brief results of our recent research on pesticide accumulation in the environment in Vietnam were described.

2. RELATIONSHIPS OF AQUATIC TOXICITY AND BIOCONCENTRATION WITH LOG P

According to Overton-Meyer lipid theory of narcosis\(^3\) that the toxicity of simple nonelectrolyte organic compounds depends specifically on their ability to partition from water to a lipid phase site of action, the narcotic activity (a kind of toxicity) for tadpoles of various organic compounds is correlated well with log P, deriving eq. 1\(^3\),

\[
\log 1/C = 0.90 \log P + 0.91 \\
n = 57 \quad r^2 = 0.93 \quad (1)
\]

where C is the minimum narcotic concentration. In eq. 1 and the following correlation equations, n is the number of compounds and r^2 is the determination coefficient. Other aquatic toxicity - log P relationships are shown in eqs. 2 and 3\(^4\). Aquatic toxicity is presented in terms of LC_{50} which is the 50% lethal concentration.

The 14-day LC_{50} (M) against guppy by various organic compounds

\[
-\log LC_{50} = 0.87 \log P + 1.13 \\
n = 50 \quad r^2 = 0.98 \quad (2)
\]

The 4-day LC_{50} (M) against juvenile fathead minnow by various organic compounds
\(-\log LC_{50} = 0.90 \log P + 1.29 \)
\(n = 150 \quad r^2 = 0.92 \quad (3)\)

The coefficients of the \( \log P \) term are close to unity and the intercept values are similar irrespective of the test organism in eqs. 1-3. It suggests the lethal effect is based on the general toxicity caused by the hydrophobicity of the compounds.

The hydrophobic compounds like dichlorodiphenyltrichloroethane (DDT) \((\log P = 6.9)\), which is an old pesticide and was listed as one of Persistent Organic Pollutants (POPs) under the Stockholm Convention\(^6\), accumulate in the fat of animal bodies and cause some toxicity for animals\(^7\).

In the south shore of Long Island, DDT and its metabolites, dichlorodiphenyldichloroethylene (DDE) and dichlorodiphenyldichloroethane (DDD) \([\text{DDT}s]\) residues in various organisms from the vicinity was investigated\(^7\). The DDTs concentration was 0.04 ppm (mg/kg) in plankton, 0.4 ppm in a kind of shellfishes, and 75 ppm in a ring-billed gull that is almost 2,000 times more than that in plankton. The concentration was increased in higher organisms.

Bioconcentration means the accumulation of chemical compounds dissolved in water into fishes and aquatic organisms through their gills and body surface directly. Bioconcentration Factor \((BCF)\) is the ratio of the concentration of a chemical compound in an aquatic organism to that in the aqueous phase under steady-state condition. The relationships between the logarithm of \(BCF\) of various compounds and \(\log P\) are shown in eqs. 4-6\(^4\).

\[ \log BCF = 1.00 \log P - 1.32 \]
\[ n = 43 \quad r^2 = 0.94 \quad (4) \]

\[ \log BCF = 1.02 \log P - 0.63 \]
\[ n = 11 \quad r^2 = 0.98 \quad (5) \]

\[ \log BCF = 0.65 \log P - 1.17 \]
\[ n = 9 \quad r^2 = 0.92 \quad (6) \]

The \(BCF\) of chlorinated hydrocarbons including DDT and \(\gamma\)-BHC (an old pesticide)

\[ \log BCF = 0.91 \log P - 1.14 \]
\[ n = 10 \quad r^2 = 0.74 \quad (7) \]

The \(BCF\) of chlorobenzenes in rainbow trout

\[ \text{BCF} \] of isoprothiolane (a pesticide) analogs in killifish

\[ \text{BCF} \] of chlorinated hydrocarbons including DDT and \(\gamma\)-BHC (an old pesticide)

The log \(P_M\) was used for prediction of \(BCF\) of ten organophosphorus pesticides in male guppies\(^{10}\). As a result, log \(P_M\) was a better index for predicting log \(BCF\) than log \(P\) as shown in eqs. 7 and 8.

Our research group proposed an alternative hydrophobicity index, a membrane accumulation index \(P_M\)\(^{10}\) using the parallel artificial membrane permeation assay, PAMPA\(^{11}\). In PAMPA, a 96-well microtiter plate completely filled with aqueous buffer solutions was covered with a hydrophobic filter coated with lipids in an organic solvent solution in a sandwich construction (Fig. 1). The permeability of a compound through the hydrophobic filter (the artificial membrane) is measured as the PAMPA permeability coefficient which is used as an index for passive transport through biomembranes\(^{12}\). As the PAMPA permeability of hydrophobic compounds was limited by their high artificial membrane accumulation, the \(P_M\) was defined as the ratio of the amount of a compound in membranes to the amount of a compound in buffer solutions in the steady state.
\[
\log BCF = 2.62 \log P_M - 1.60 \\
n = 10 \quad r^2 = 0.95 
\]

Although a number of measured \( P_M \) data is limited and therefore it is currently difficult to theoretically calculate \( P_M \) values of various compounds like \( P \), \( P_M \) may be useful for prediction of \( BCF \) of other groups of compounds.

3. OUR RESEARCH ON PESTICIDE ACCUMULATION IN VIETNAM

Many pesticides are hydrophobic and likely remain in the environment if they are not appropriately used. Several years ago, our research group have heard from a Vietnamese professor about the overuse of pesticides and people’s anxiety for food safety in Vietnam. The author also found a news about long-standing pesticide overuse in Vietnam on the VNExpress News website\(^{13}\). Thus, we started the research on pesticide use and residue analyses in the environment in Hue at the central Vietnam. Hue was the national capital in the past and agricultural products are mostly not exported, but consumed domestically in Hue.

As described above, aquatic organisms may accumulate hydrophobic pesticides. We have visited Hue since 2014 and taken shellfish samples as well as soils and sediments to measure pesticide residues contained in the samples. Those shellfishes were not cultured, but people eat them. If the shellfishes accumulate pesticides, healthy problems may be caused for the people who eat them. Several pesticides were detected, but the accumulation was not found in soils and sediments. I explain the results about shellfishes in the details below.

Firstly, shellfishes which inhabit in canals in Huong Chû Commune at the mountain side area near Hue city were taken in 2014-2015\(^{14}\). Several pesticides such as imidacloprid, fenobucarb and emamectin benzoate were detected in the shellfish samples. The residue concentration of emamectin benzoate (unpublished data) in a few samples was more than the maximum residue limit (MRL) in shellfish in Japan, 0.5 ppb\(^{15}\). The hydrophobicity of emamectin benzoate is high (\( \log P = 5.0 \)) although the pesticide is rapidly degraded in the environment\(^{16}\).

Secondary, the pesticide residues in the shellfishes taken in Huong Phong Commune at the sea side area were measured in 2018-2019 (Fig. 2). As not only the agriculture (rice) but also aquaculture was carried out in this area, many shellfishes inhabited in the lagoon, canals, and ponds. If the shellfishes accumulate pesticides, cultured fishes, crabs and shrimps may also contain pesticide residues. As a result, pesticide residues were detected in several shellfish samples. The detected amount of the pesticides was compared with their acceptable daily intake (ADI)\(^{17}\) in order to evaluate the risk by the pesticide residues. The ADI is the estimate of the amount of a pesticide in food or drinking-water that can be ingested daily over a lifetime without appreciable health risk to the consumer. The ADI (mg/kg weight/day) value of each pesticide is defined as 1/100 of the no-observed adverse effect level (NOAEL) of the pesticide which was obtained from the various toxicity tests against various animals. Consequently, there was no risk of the detected pesticides for humans. Emamectin benzoate was not detected in shellfishes although this pesticide was frequently used in the area.

Fig. 2  A farmer who is taking shellfishes in Huong Phong Commune, Photo taken by Akamatsu on August, 2019

4. CONCLUSION

The hydrophobicity of a chemical compound is an important property for the prediction of the aquatic toxicity and bioaccumulation of the compound in the environment. The log \( P \) and log \( P_M \) were used as the indices of hydrophobicity. The long-standing pesticide overuse is considered as a problem in Vietnam. Many pesticides are hydrophobic and may accumulate in the environment and in the aquatic organisms. Therefore, the research on pesticide residue analyses in shellfish samples taken in Vietnam was carried out. As a result, pesticide residues were detected in several shellfish samples, but the residues were at the level that there was no risk for humans.

The author found many wasted pesticide packages discarded in agriculture fields during the research period (Fig. 3). The packages possibly
cause a pollution problem in the environment. According to the overview of regulations on chemical management and environmental protection in Vietnam in 2018\textsuperscript{81}, Vietnamese Ministry of Natural Resources and Environment is planning to revise the law on environmental protection such as collection and destruction of pesticide packaging. The chemical management in Vietnam is supposed to be improved in the near future. However, the similar situation related to the pesticide use may occur in other developing countries where the economy is rapidly growing. We should carefully watch the pesticide use in such countries.

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