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ESTABLISHING PROCESSING FACTORS FOR FAT SOLUBLE PESTICIDES IN CRUDE VEGETABLE OILS AND FATS

EU Regulation No. 396/2005 sets maximum residue levels (MRLs) for raw agricultural products, like oilseeds/oil fruits. MRLs for pesticides in processed products like crude oils (and refined oils) are not specifically set in EU legislation. According to Article 20 of Regulation No. 396/2005, MRLs for pesticides in processed products have to be derived from the MRLs for raw agricultural products, taking into account the concentration or dilution caused by processing (**processing factor**).

In the oil extraction process, the concentration/dilution factors depend on the type of processing and the extent to which meal and crude oil pick up a specific pesticide during crushing. The solubility of a pesticide in water or fat, and in the solvents used in oil extraction, influences the concentration of a pesticide in the processed products.

For the reasons mentioned above, research is in theory the only way to establish the processing factors accurately. In practice, it is however not feasible to carry out a research study to set processing factors for all pesticides/processed products combinations. This would indeed take an excessive amount of time considering the number of pesticides used today (several hundred pesticides) and the types of crude oils of economic interest to the oil industry (about 20).

In the case of **crude oils**, maximum residue levels can be approximated based on the physico/chemical properties of the pesticides and on the oil content of the raw materials. *Pesticides with high solubility in fat (or in the extraction solvents) will concentrate in crude oil*. *In this case, the MRL for crude oil will be the seed MRL multiplied by a processing factor*. This factor is inversely related to the oil content of the seed or lower. Table 1 gives some theoretical processing factors from seed/fruit to crude oil during crushing to be applied for fat/hexane soluble pesticides.

168, avenue de Tervuren (bte 12) ● B 1150 Bruxelles ● Tel (32) 2 771 53 30 ● Fax (32) 2 771 38 17 ● Email : fediol@fediol.be ● http://www.fediol.be

Table 1*: processing factors to be applied for fat/hexane soluble pesticides

Oil seed	Average oil percentage	Processing factor
Rapeseed	40-45	2,5
Sunflower seed	40-45	2,5
Soybean	18-21	5
Coconut (as it is for fruit incl. coconut water)	20	5
Palm fruit	50-55	2
Palm kernel	45	2
Groundnut/peanut	40-50	2,5
Linseed	40-50	2,5

*the content of this table will be updated as new information/data becomes available

Knowing whether a pesticide has high solubility in fat is therefore very important. Over the last years, FEDIOL has explored the concept of **fat solubility** and has identified two main elements allowing to give an indication of the fat solubility of an active substance:

1. The **octanol/water partition coefficient (P_{ow} or K_{ow})** is the extent to which a substance partitions between octanol and water. It is defined as the ratio of the concentration of the substance in the octanol phase[1] divided by the concentration in the water phase. The logarithmic value of this coefficient is an important physico-chemical parameter that can be used to predict whether a substance is water or fat-soluble. Historically[2], pesticide experts have looked into this parameter in the context of the setting of MRLs in animal commodities (meat, animal fat & edible offals) when information on the distribution of pesticides from metabolism or feeding studies was not allowing an assessment of the fat solubility to be made. The solubility of a pesticide in animal tissues is indeed dependent on its solubility in water and organic solvents since animal tissues have different water and organic contents. In this context, pesticide experts came to the consensus that pesticides having a log P_{ow} value of 3 or above would be considered as "fat soluble" (while those having a log P_{ow} value below 3 would not). This value of "3" was derived from a calculation in which the distribution of the pesticide between muscle and fat was derived from the log P_{ow} value of the substance, and in which the lipid and water fractions in each of these two compartment were considered. Getting back to the behavior of pesticides during the vegetable oil processing, FEDIOL experts believe that a log P_{ow} value of 3 (which was determined in a very specific context not directly transposable for vegetable oil processing) should not be seen as an absolute value to define what is "fat-soluble".

[1] Octanol is a common surrogate for organic phases.
[2] FAO (Food and Agriculture Organization of the United Nations), 2005. Report of the Joint Meeting of the FAO Panel of Experts on Pesticide Residues in Food and the Environment and the WHO Core Assessment Group on Pesticide Residues Geneva, Switzerland, 20–29 September 2005. http://www.fao.org/fileadmin/templates/agphome/documents/Pests_Pesticides/JMPR/JMPR05report.pdf

Looking at the definition of the octanol-water partition coefficient (see info box below), and as shown in recent experiments carried out by FEDIOL, it would probably be wrong to assume that pesticides with a log P_{ow} < 3 would not be found in crude oil. Pesticides having a log P_{ow} value between 1 and 3 may in fact mostly concentrate in the oil after crushing (although not totally).

The octanol-water partition coefficient

The octanol/water partition coefficient (P_{ow} or K_{ow}) is the extent to which a substance partitions between octanol and water. It is defined as the ratio of the concentration of the substance in the octanol phase divided by the concentration in the water phase.

$$P_{ow} = C_{octanol} / C_{water}$$

It provides an estimate of the tendency of a substance to bioaccumulate in fat (see examples listed in Table 2).

Table 2: examples of calculation of log P_{ow}

Examples	$C_{octanol}$	C_{water}	P_{ow}	log P_{ow}	% in octanol
1	1	1	1	0	50,0%
2	10	1	10	1	90,9%
3	100	1	100	2	99,0%
4	1000	1	1000	3	99,9%

- Any chemical with a log P_{ow} of 3 or greater will bioaccumulate in fat. A value of 3 means that the substance is 1000 times more soluble in octanol (and theoretically, fat) than in water.
- Any chemical with a log P_{ow} of 1 or greater will bioaccumulate in fat but to a lesser extent. A value of 1 means that the substance is 10 times more soluble in octanol (and theoretically, fat) than in water.
- Any chemical with a negative log P_{ow} is not considered to bioaccumulate in fat.

2. "**F**": this letter is attributed to certain pesticides in the EU pesticide database[3] when pesticides have been assessed and defined as "fat soluble". This qualifier follows an assessment where all relevant data have been considered. For this reason, a compound with a relatively high log P_{ow} value may well be considered as "non-fat soluble" based on other elements (such as metabolism or feeding studies). Example: fenbuconazole, which has a log P_{ow}= 3.8, is not attributed an F in the EU pesticide database.

In practice

In view of the above considerations, as well as of recent experiments carried out by FEDIOL, the fate of a pesticide during **crushing** can pragmatically be predicted as follow:

- When the log P_{ow} (or log K_{ow}) exceeds 3 or when the substance is identified as "F" in the EU pesticide database: it is reasonable to assume that the pesticide will totally concentrate in the oil after crushing. In this case, the MRL for crude oil corresponds to the seed MRL multiplied by the theoretical processing factor (Table 1).

[3] http://ec.europa.eu/food/plant/pesticides/eu-pesticides-database

- When the log P_{ow} (or log K_{ow}) is between 1 and 3 (and in absence of other specific data): it is reasonable to assume that most of the pesticide will concentrate in the oil after crushing, even though not totally. In this case, the seed MRL multiplied by the corresponding theoretical processing factor (Table 1) gives a good approximation of the MRL in crude oil.
- When the log P_{ow} (or log K_{ow}) is negative, it is reasonable to assume that most of the pesticide will concentrate in the water phase.
- In absence of information regarding the log P_{ow} value of a substance (and if the substance is not attributed an F in the EU database), another factor that can be considered is the affinity of the substance for the extraction solvent. Some pesticides can show the tendency to concentrate in the oil due to their solubility in solvents like e.g. hexane. Pesticides with a significant solubility in organic solvents as compared to water will follow the fat phase.
- In case no information on a substance is available, in-house data (such as QSAR modelling[4]) are decisive.

Remarks

- When the pesticide residue definition covers different substances (parent and metabolites incl. isomers), the fat solubilities of these substances may be different. In such case, information on the log P_{ow} of each individual substance should be considered if available.
- The possible concentration effects of processing should be taken into account also in the cases when the MRL is set at the limit of determination (LOD). The reason for this is that in some case, undetectable traces of a substance might be present in the seeds, and concentration during processing might lead to detection of a residue in the crude oil.

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[4] http://www.ecetoc.org/report/estimated-partitioning-property-data/computational-methods/log-kow/