

Endocrine Disrupting Chemical (EDC) Retention Framework

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Background and Theory

A number of chemicals of emerging concern, including pesticides and herbicides, antibiotics used in animal agriculture, and growth-promoting hormones, are associated with agricultural activities. Many of these chemicals have, or are suspected of having, properties that affect or disrupt endocrine systems. These endocrine-disrupting chemicals (EDCs) may be applied directly to crops or the soil, or are present in manures that are applied to soils. Consequently they have the potential to be transported into surface waters by surface runoff or through tile drains.

Because many of these chemicals are strongly associated with soil solids, they are transported mainly as chemicals sorbed to suspended sediment, not as chemicals dissolved in water.

Many of these chemicals are hydrophobic and thus have a strong affinity for organic matter. This is expressed by the K_{OC} value (the distribution coefficient between the aqueous phase and organic carbon (OC)). This is a commonly measured parameter for organic chemicals in soil environments because it normalizes sorption in soils having varying properties to a single value.. If you know the K_{OC} value for a chemical and the OC of organic matter (OM) content of the soil, you can determine the distribution of the chemical between the aqueous phase and the soil-sorbed phase.

Calculations

The distribution coefficient (K_D) is determined as:

$$K_D = K_{OC} * X$$

where

X = the unitless fraction of organic C in the soil.

If the soil OM content is known, you can assume that OM is approximately 50% carbon by weight, and therefore $OC \approx OM/2$. For example, if a soil has 4% organic matter, $X = 0.02$.

The distribution coefficient for a specific chemical can then be used to determine its distribution between the aqueous and sorbed phases at equilibrium:

$$K_D = C_{sorbed} / C_{aq}$$

where

C_{sorbed} is the sorbed concentration ($\mu\text{g kg}^{-1}$),
 C_{aq} is the concentration in solution ($\mu\text{g L}^{-1}$), and
 K_D is the distribution coefficient (L kg^{-1})

Typically we know the total concentration in the soil, not the concentration in either of the two phases. The following relationship then applies if the total concentration is on a soil dry weight basis:

$$Q_{total} = Q_{sorbed} + Q_{aq}$$

where

Q_{total} is the total quantity (μg) of the EDC
 Q_{sorbed} is the quantity sorbed to soil, and
 Q_{aq} is the quantity dissolved in water

$$Q_{total} = C_{sorbed} * Soil (kg) + C_{aq} * H_2O (L)$$

If the total concentration is on a soil dry weight basis, then for 1 kg of soil (dry wt) we get:

$$C_{total} = C_{sorbed} + C_{aq} * V$$

where

V is the volume of water associated with 1 kg of soil

rearranging the distribution equation, we get:

$$C_{aq} = C_{sorbed} / K_D$$

and can then substitute for C_{aq}

$$C_{total} = C_{sorbed} + (C_{sorbed} / K_D) * V$$

This can be rearranged to:

$$C_{total} = (1 + V/K_D) * C_{sorbed}$$

and solved for C_{sorbed}

$$C_{sorbed} = C_{total} / (1 + V/K_D)$$

which is the concentration of the chemical sorbed to the particulate phase.

For chemicals with high K_{OC} values, $C_{sorbed} \approx C_{total}$

If we wish to know the concentration in the aqueous phase, we can go back to the distribution equation to get:

$$C_{aq} = C_{sorbed} / K_D$$

Once we know the concentration of a chemical on the particulate phase, we can proceed to determine the quantity of that chemical that is retained by conservation practices. The quantity of a chemical that is retained by perennial grassland conservation practices can be estimated by multiplying C_{sorbed} times the mass of sediment retained by perennial grasslands. We can use the new erosion estimators developed in the ENRTF-funded project *Measuring Conservation Practice Outcomes* to determine the mean annual difference in sediment losses between a tilled field and the same field planted to perennial grasslands. Once we have obtained those values, we determine the difference between the two and multiply that by C_{sorbed} to yield the quantity of chemical retained by conservation practices on an annual basis.

The associated spreadsheet, EDC Estimator.xls, provides those estimations if provided with the appropriate inputs.

Caveats:

Although we now have an estimator to calculate the percentage or total quantity of EDCs applied to agricultural fields, there are limitations to its use and its capabilities.

1. *Hydrophilic compounds* - The distribution coefficient, K_D , can only be determined accurately from K_{OC} values for hydrophobic organic chemicals. Chemicals that have more of a hydrophilic character will tend to distribute more to the aqueous phase unless they are retained by charged sites such as clay minerals. More accurate determination of the distribution coefficients of these chemicals may require actual determination of their K_D s on a site-by-site basis.

2. *Determination of V, the effective water-to-soil ratio* - Determination of the ratio of water to soil used in the calculation is fairly subjective. Most individuals using these concepts are interested in the quantity of chemical in a known volume of water and simply view the soil as a source. Because we are interested in what remains on the soil and don't know the volume of water involved, it is more difficult to accurately pin down the water-to-soil ratio.

In general, hydrophobic EDCs are slow to reach equilibrium between the soil and aqueous phases when the solid phase is mixed with water or if additional water is added to a suspension. For soil water (water held within the pores of the soil), and perhaps drainage water that has slowly leached through the soil under the influence of gravity, EDCs may be in, or approaching, equilibrium with the soil-sorbed phase. This represents a fairly small water-to-soil ratio,

however, as soil water generally constitutes less than 50% of the total volume of soil; on a volume-to-mass (L kg^{-1}) basis this would be approximately 0.77 L kg^{-1} if we assume a bulk density of 1.3 for the soil.

Likewise, we seldom have more than 10 to 20 cm of water draining through our soils on an annual basis. If we assume 20 cm of drainage water, that would be the equivalent of $200 \text{ L m}^{-2} \text{ yr}^{-1}$. A square meter of soil 10 cm thick would weigh approximately 130 kg, so the combined ratio of water to soil would be 50 L soil water + 200 L drainage water divided by 130 kg soil, or a ratio of slightly less than 2 : 1.

Sediments eroded by water are much more dilute, with water-to-soil ratios as high as 100 : 1 or even higher. However, the contact time between erosive waters and sediment during transport is fairly short (often only a matter of minutes to hours) and it is unlikely that the eroding waters would come close to achieving equilibrium with the sediments they are transporting.

Because the large volume of water in contact with the soil during erosion does not maintain contact long enough for the EDCs to reach equilibrium with this large water-to-soil mixture, use of the actual water-to-soil ratio would greatly over-estimate C_{aq} , the concentration of EDCs in the aqueous phase. Based on these assumptions, this estimator uses an "effective volume of water", V^{\dagger} , to estimate the quantity of EDCs in the aqueous phase. The current figure for V^{\dagger} is a water-to-soil ratio of 10 L : 1 kg. Further survey of the literature may yield a better estimate of the water-to-soil ratio, and the estimator can be modified accordingly.

3. Chemical persistence - The persistence (half life, $t^{1/2}$) of EDCs varies considerably. Some are highly persistent with half lives of many years, while others have half lives of less than a year. Consequently, the concentration that is applied may not represent the concentration in the soil at a later date when erosion might occur.

Transport in the aqueous phase must occur within a timeframe corresponding to the relative persistence of the compounds. However, since many of these chemicals are applied annually or more frequently, their concentrations are often maintained over long periods of time.

4. Presence and concentration - This is probably the single largest problem with use of the estimator. There are numerous agricultural chemicals that are applied at varying rates. Because record-keeping is not required for use of these chemicals, it is impossible to estimate the concentration of any specific chemicals or to determine where they have been applied. Regional usage figures may be available from the Minnesota Department of Agriculture or other sources, and application rate information is available for some of the chemicals from the manufacturers, so general estimates of usage and concentrations may be possible, but determination of site specific application rates or concentrations is not generally possible.

Data Requirements

Data required to determine quantities (mass) of EDCs retained by perennial grassland conservation practices:

General Parameters

- % OM in surface soils ⁽¹⁾
- V^* , the water to soil ratio ⁽²⁾

Site Specific Parameters

- Quantity of sediment retained by conversion to perennial grasses ⁽³⁾

Chemical Specific Parameters

- K_{OC} ⁽⁴⁾
- Mean concentration in soils ($\mu\text{g}/\text{kg}$) ⁽⁵⁾
- $t^{1/2}$ (half life) ⁽⁶⁾

⁽¹⁾ Can be estimated from Estimators data or can be determined from the NRCS Soil Survey.

⁽²⁾ See discussion above.

⁽³⁾ Main product of the Sediment Retention Estimator.

⁽⁴⁾ From the literature.

⁽⁵⁾ From literature or can be estimated from known application rates.

⁽⁶⁾ From the literature. (Not a required parameter, but can be useful in estimating the mean concentration in soils)

The *relative potential reduction* in EDCs (% of applied EDCs that are retained by perennial grassland conservation practices) can be estimated without knowledge of either the concentration of EDCs applied or the mass of soil retained by the conservation practices. The attached spreadsheet, EDC Estimator 2.xls, provides those estimations.

Appendix 1

K_{OC} values for selected potential endocrine disrupting chemicals.

Chemical	K _{OC}	Reference
acetaminophen	41	Toxnet HSDB
atrazine	51-243	Chen et al. (1984) reported in Agertved et al. (1992)
	26-1,164	Toxnet HSDB
carbamazepine	510	Toxnet HSDB
carbaryl	290	USDA ARS
daidzein	833	EPI Suite estimate (KOW)
	2,329	EPI Suite estimate (MCL)
	1	Schenzel et al 2012 (expt, NOM)
	6,500	Toxnet HSDB
equol	23,988	EPI Suite estimate
	1,029	Yost et al. (2013) (average of 6 measurements)
erythromycin	1,645	Jones et al. (2002)
17-b-estradiol	1,349-4,898	Carballa et al. (2008)
	3,981	Lai et al. (2000)
genistein	6,500	Toxnet HSDB
metolachlor	22-2,320	Toxnet HSDB
monensin	10	Toxnet HSDB
oxytetracycline	42,506	Rabolle and Spliid (2000)
	47,881	Rabolle and Spliid (2000)
	93,317	Rabolle and Spliid (2000)
	27,792	Rabolle and Spliid (2000)
17-alpha-trenbolone	588	Blackwell et al. (2012)
	420	FDA Animal Veterinary Approval
	477	FDA Animal Veterinary Approval
	1,100	FDA Animal Veterinary Approval
	400-9,500	Syntex Material Safety Data Sheet
17-beta-trenbolone	1,010-9,570	Roche Safety Data Sheet

tylosin	7,988	Rabolle and Spliid (2000)
	771	Rabolle and Spliid (2000)
	5,664	Rabolle and Spliid (2000)
	553	Rabolle and Spliid (2000)
virginiamycin	980 (M1)	Toxnet HSDB
(virginiamycin has two components: M1 and S1)	160,000 (S1)	Toxnet HSDB

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