

## PESTICIDE RETENTION IN THE WATERSHED AND IN A SMALL CONSTRUCTED WETLAND TREATING DIFFUSE POLLUTION

K. Haarstad\* and B.C. Braskerud\*

\* *Jordforsk (Norwegian Centre for Soil and Environmental Research)*  
*Frederik A. Dahls vei 20, N-1432 Ås, Norway*  
(E-mail: bent.braskerud@jordforsk.no; ketil.haarstad@jordforsk.no).

### ABSTRACT

Loss of pesticides is likely from watersheds where pesticides are used. The herbicides propachlor, linuron and metamilon, and the fungicides propiconazole, fenpropimorph and metribuzin and metalaxyl, were applied on an arable soil plot. A mass balance study showed that approximately 96 % of the applied pesticides disappeared within the watershed. Three pesticides remained as residuals in the soil profile one year after the application. The 4 % of the pesticides that were lost from the watershed gave peak concentrations, appearing immediately after spraying, reaching levels that can be hazardous to aquatic life. The constructed wetland situated in the first-order stream generally managed to lower the peak concentrations significantly. For the summer season, retention varied from 12 to 67 % the first year. The second year, we observed both loss and retention. Increasing the wetland surface from 0.2 % to 0.4 % of the watershed area increased the average retention with 21 % units the first year and 9 % units the second year. Chemical properties of the pesticides could explain some of the behaviour in the watershed and in the wetland.

**Keywords: Best management praxis; degradation;  $K_{oc}$ ; half-life; non-point source pollution; pesticides**

### INTRODUCTION

Pesticide loss to the environment is unattractive because of possible environmental hazards. Modern pesticides degrade or sorb in nature because of processes such as sedimentation, sorption to mineral and organic particles, uptake and adsorption to organisms, biological degradation, photodegradation and volatilisation. In a previous paper we screened the retention of 13 pesticides in a constructed wetland (CW), to evaluate small wetlands as a possible way to mitigate pesticide loss from arable land (Braskerud and Haarstad, 2003).

Here, we present results from a 19 month study simulating loss of pesticides from a field with vegetable crops, measuring pesticide concentrations in the arable soil and in the same free water surface (FWS) CW. Wetland size influence construction costs greatly, so the effect of CW area is important to investigate. We also investigated whether chemical properties of the pesticides such as sorption, degradation and water solubility, influence the retention.

### MATERIALS AND METHODS

*The sampling program, analyses, wetland and watershed, were detailed in Braskerud and Haarstad (2003) and Braskerud (2001).*

#### The wetland

The wetland Grautholen is located about 45 km south of Stavanger on the south-western coast of Norway. The wetland was built in 1993 by expanding the stream banks, creating a surface area of 840 m<sup>2</sup>. The CW contains a sedimentation pond in the inlet (0.5 m deep), followed by three wetland filters (0-0.3 m), three surface flow zones (0 m), and a wetland filter with a V-notch in the outlet. Sediments were high in organic content (18-37 % as loss of ignition). The wetland is covered with vegetation.

#### The watershed

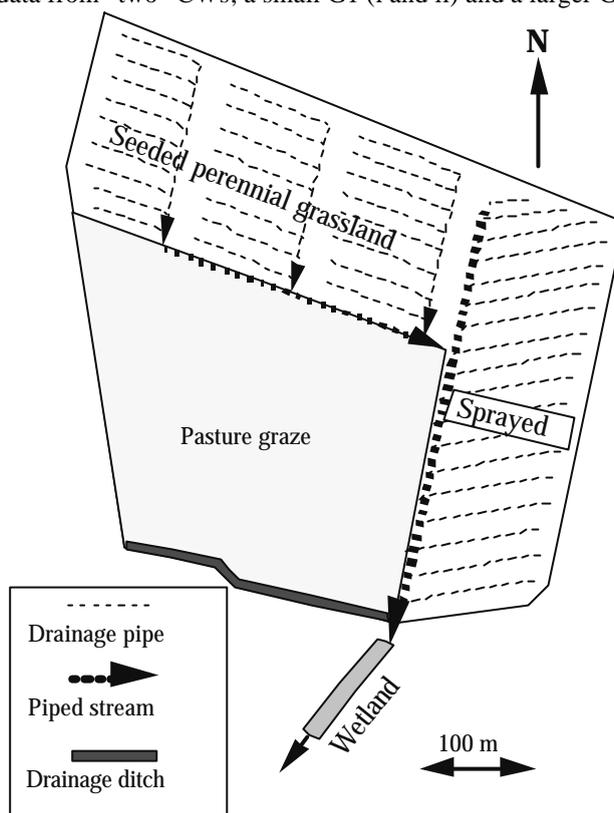
Water from a 22 ha watershed enters the wetland. The soil consists of silty moraine with a clay content of 6%. The loss of ignition in the topsoil varies from 6 – 27 %. The former stream is led through drainage pipes. The drainage pipes are located at 0.8-1.0 m depth. The whole area is used for agricultural production (Fig. 2). On average, the annual loss of soil particles, nitrogen, and phosphorus were 820, 48 and 4.0 kg ha<sup>-1</sup>, respectively (Braskerud, 2001). The pH in the topsoil varied from 5 to 6.3, and in the stream water from 6.3 to 7.7.

#### Adding pesticides

We applied pesticides on the arable field to let natural retention processes in the watershed influence the leakage (Fig. 1 and Table 1). Previous research (Braskerud, 2001; 2002) have shown that the retention in CWs is highly influenced by the watershed. The dose added was equal to the recommended dose for 0.2-6.1 hectares. Usually, the pesticides were added once, on May 26<sup>th</sup> and 30<sup>th</sup> for the years 2000 and 2001, respectively. The same area was used for spreading the pesticides both years.

**Water flow measurement and sampling equipment**

The V-notch weir in the dam outlet recorded the discharge by logging a pressure gauge. The logger controlled a water flow proportional *composite sampling* system in the inlet (i), after the 3<sup>rd</sup> wetland filter half way through the CW (ii), and the outlet (iii). Hence, we received data from “two” CWs; a small G1 (i and ii) and a larger G2 (i and iii).



**Figure 1.** Originally the watershed was used for grass production. Pesticides used in vegetable production were sprayed on 0.1 hectare ploughed land right of the piped stream.

**Soil sampling from the wetland sediment and sprayed area**

Three samples from the *topsoil* (0-0.2 m), and the *subsoil* (0.5 and 0.8 m) were taken from the sprayed area (Fig. 2), and made up one composite sample per depth. Reference samples from the non-sprayed area, close to the sprayed area, were also taken. *Sedimentation plates* made of 25 x 25 x 1 cm plastic coated plywood were placed in the wetland filters. Soil and sediment sampling was carried out on the 30<sup>th</sup> May 2001, before the second addition of pesticides.

**Sampling and analyses**

Norwegian standard methods were used for measurement of total suspended solids (TSS), total phosphorus (TP) and total nitrogen (TN). Organic particles (org-SS) were the loss of ignition of TSS.

Two multi-methods were used for pesticides in water and sediment:

- *M03*: Pesticides were preserved in the field by adding 25 mL dichloromethane to 500 mL of water in a glass bottle and stored at 4 °C until analysis. The samples were extracted with dichloromethane, and analysed by GC with NP-EC (Holen and Christiansen, 2001).
- *M54*: Soil and sediment samples were stored at -18°C until analysis. Ten g of wet material was extracted twice with methanol (20 mL + 20 mL), and the extracts combined. An aliquot of 4 mL was analysed as described for the water samples (Holen and Christiansen, 2001).

**Table 1. Compound characteristics (Tomlin, 1994; ASRUSA; Ludvigsen and Lode, 2001; Chemfinder) \***

Pesticide	Type	$K_{oc}$	$T_{1/2}$	Wat.S.	pKa	Photod.	MAL	PI
fenpropimorph	F	3.43	60	4	7.0	stable	0.45	1.1
linuron	H	2.70	82	75		49-300	0.07	2.2
metalaxyl	F	2.23	80	8400		156	280	4.1
metamitron	H	0.85	30	1800		rapid	1.10	1.4
metribuzin	F	1.72	47	1050	1.0	0.2-15	0.22	1.5
propachlor	H	1.90	12	700		227	0.29	1.1
propiconazole	F	2.80	53	110	1.1	250	0.02	2.2

\*Type = Herbicide, Fungicide.  $K_{oc}$  (log) is used because  $K_d$ -values are less frequently reported in the literature. Half-lives ( $T_{1/2}$  and Photodegradation in water, in days). Wat. S. = water solubility at 20 or 25°C ( $mg\ l^{-1}$ ). MAL = Maximum allowable concentration in water ( $\mu g\ l^{-1}$ ). PI = polarity index (see text).

## RESULTS AND DISCUSSION

### Where is the largest pesticide sink?

It is possible to track the individual pesticides through a mass balance study in the watershed – wetland system (Table 2). The runoff of pesticides applied in May 2000 was investigated for 12 month before soil sampling, and the start of a new growing season. Results show that only a minor part of the applied pesticides leaves the watershed. Retention processes in the watershed itself removed approx. 89 % of the pesticides. None of the variables in Table 1 were correlated to “retention

**Table 2. Occurrence of pesticides in the watershed from May 2000 to May 2001.**

Pesticide	Applied to watershed		Residual in soil (%)	Loss from watershed (%)	Retention in CW (%)#	Retention in watershed (%)♣
	(g)	(%)				
fenpropimorph	2250	100	6.8	0.3	0.1	92.9
linuron	900	100	0	3.1	0.8	96.9
metalaxyl	2880	100	2.3	6.7	2.0	91.0
metamitron	2800	100	0	4.6	2.6	95.4
metribuzin	353	100	0	9.4	3.1	90.6
propachlor	1560	100	0	3.8	2.6	96.2
propiconazole	750	100	36.8	3.0	0.3	60.2
Average		100	6.6	4.4	1.6	89.0

# Retention in wetland G2.

♣ Retention in watershed equals applied pesticide subtracted pesticides in soil, and loss from watershed.

### Adsorption to the soil

Only three pesticides remained as significant soil residues (Fig. 2). The fungicides and linuron generally adsorb better than the herbicides (see  $K_{oc}$ , Table 1). Metalaxyl is special with a high water solubility and high  $K_{oc}$ -value.

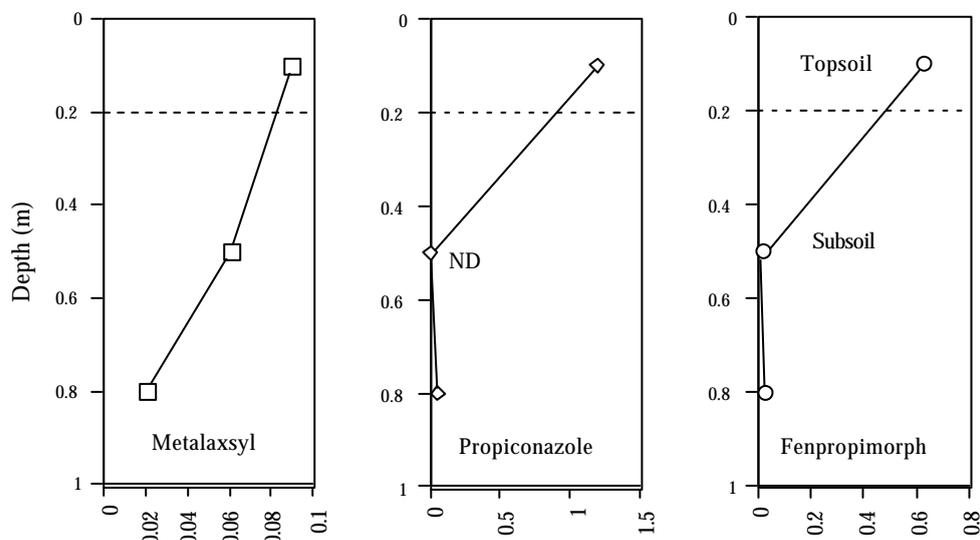
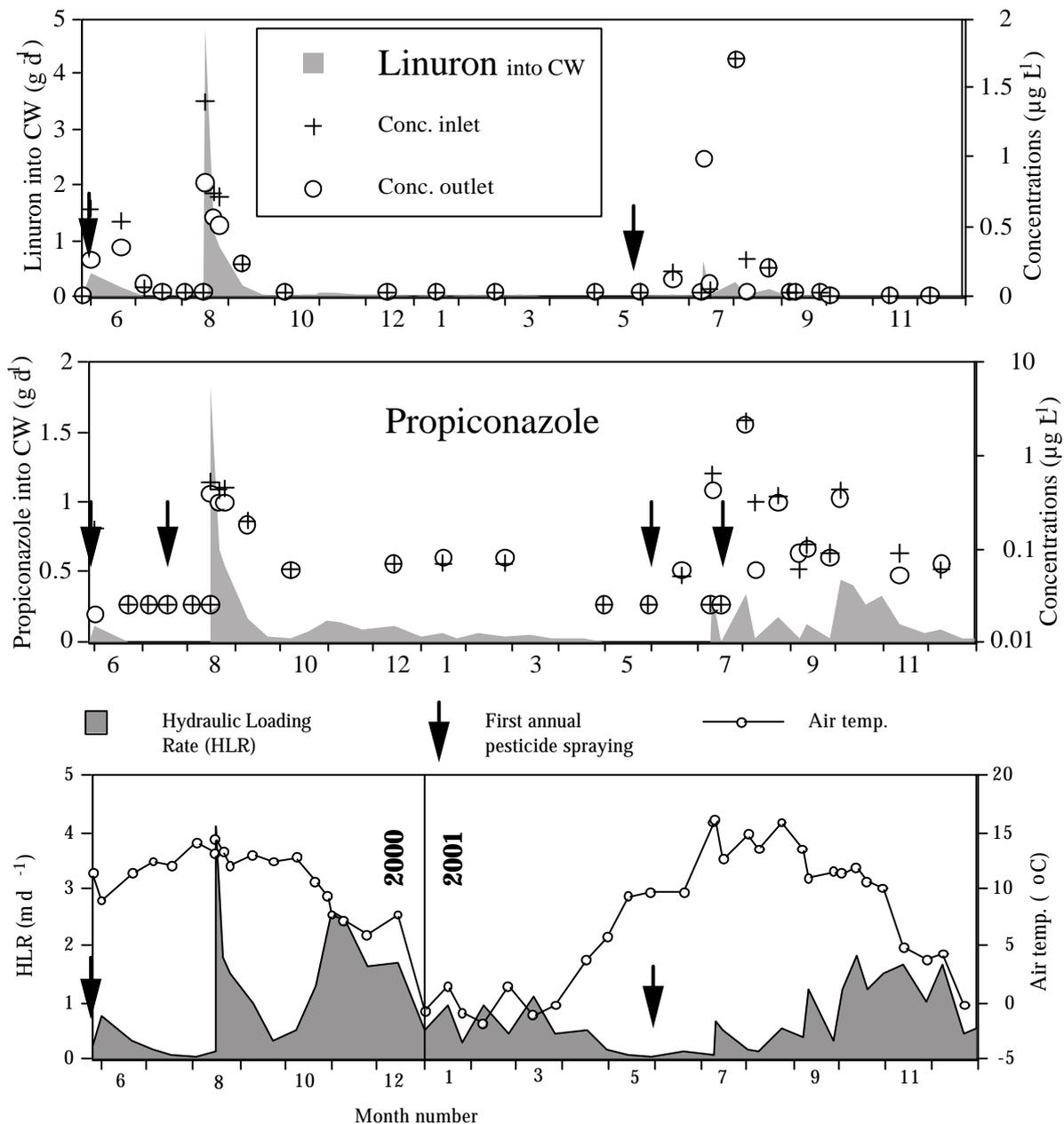


Figure 2. Pesticides (mg per kg DW soil) in the soil on May 30, 2001, one year after application (ND = not detected).

If soil density is assumed to be  $1.0 \text{ kg L}^{-1}$  in the topsoil, and  $1.4 \text{ kg L}^{-1}$  in the subsoil, the residues of metalaxyl, fenpropimorph and propiconazole are 66 g, 153 g and 276 g, respectively. No residues from linuron, metamitron, metribuzin or propachlor were found. Spliid (2001) found fenpropimorph to be almost immobile in a sandy loamy soil. The risk for leaching was found to be in the order of metalaxyl > linuron > metamitron in a study by Kookana et al., (1995). He also found a half-life of linuron of 219 d, significantly higher than the value in Table 1. It is difficult to explain why linuron was not detected in the soil. Physical factors such as adsorption, degradation and solubility are, however, generally highly site dependent.

### Runoff from the watershed

Approx. 4 % of the applied pesticides leached out of the watershed in 2000/01 (Table 2). Loss of pesticides usually followed the runoff (or hydraulic load, lower panel in Fig. 3) until the available amount was washed out. The largest loss and the highest concentrations were observed within 4 months of application.



**Figure 3.** Loss of two pesticides from the watershed; mass transport and concentrations throughout the investigation. Concentrations in the inlet and outlet, and hydraulic load (HLR) for the wetland G2. The HLR is runoff ( $Q$ ) on CW surface area ( $A$ );  $QA^{-1}$ .

The loss of linuron, metalaxyl, metamitron and propachlor from the watershed decreased 67-98 % compared to that of the year 2000 (Table 3), even though nearly the same amount was added both years. This could be caused by adaptation of the microflora in the soil, giving an increased degradation of the pesticides the second year. Examples of such adaptation are numerous in the literature. There might also have been extra time for degradation due to little precipitation and reduced leaching the first two weeks after spraying in 2001 (Fig. 3).

For other pesticides, the situation was rather opposite: Metribuzin was only used the first year. Still, loss was also detected the next summer (Table 3). Conn et al. (1996) found that 5% of the applied metribuzin was found in subarctic soil 468 d after application, but only 1% reached a depth of 22.5 cm. The loss of propiconazole and fenpropimorph were almost the same in both years. These fungicides were, however, spread twice per season. Fenpropimorph and propiconazole are regarded as persistent, and have been used as «tracer» in some investigations on pesticides, although their half-lives are not so long (Table 1).

In this study, the most mobile compounds were metribuzin, metalaxyl and metamitron, while fenpropimorph was found in the smallest quantities (Table 2 and 3). Metalaxyl is rather interesting; it has relatively high  $K_{oc}$ -values, it is very water-soluble and degrades rather slowly. As a result, we find it both in the soil and in the water.  $K_{oc}$  was the variable that explained the pesticide loss best; as the  $K_{oc}$  -value increases the loss decreases ( $r=0.61$ ). The effect was, however, not statistically significant ( $P=0.14$ ). Compounds vary in water solubility and sorption due to e.g. humic substances in the soil and water. The polarity can, according to Torrents et al., 1997, be estimated by the polarity index (PI) derived from O + N/C (atoms). However, neither  $T_{1/2}$ , water solubility nor PI correlated with the relative pesticide leaching in Table 2.

### Retention in the CW

Less than 2 % of the applied pesticides were retained in the wetland (Table 2). In spite of this, the wetland had an important effect in lowering the peak pesticide concentrations that can be harmful for aquatic life. The maximum acceptable limit (MAL) was exceeded for six pesticides during the investigation (Table 3). Even though the application of pesticides was rather intensive compared to the recommended use, the peak concentrations measured in this study were below those found in a national agricultural and environmental monitoring program, JOVA (Ludvigsen and Lode, 2001) In 2000, the average retention of the pesticides was 21% for G1, and 42% for G2 (Table 3). The next year, however, retention generally decreased. The average retention was -1 % and 8 % for G1 and G2, respectively. Higher retention was achieved in 2000 compared to 2001 in spite of a lower average detention time the first year (approx. 7 and 10 hours for G2, respectively), indicating that concentration is more important for retention than time. A similar decrease in TSS, phosphorus and nitrogen retention could not be observed. The average hydraulic load in G1 and G2 was relatively high, 0.9 and 0.5  $m d^{-1}$  in 2000, for G1 and G2, respectively. From this point of view, the retention is considerable.

### Effect of concentration:

The decrease in pesticide retention can be due to lower input concentrations in the second year. Braskerud and Haarstad (2003) found increased retention with increasing metamitron and metalaxyl concentration. For 11 other pesticides, concentration did not have any statistically significant effect. It was, however, a strong correlation between increased conductivity and increased retention of three pesticides (fluroxypyr, linuron, and metribuzin). Could this indicate increased retention when the nutrients increase? Electrical conductivity depends on metal cations, anions and organic matter. Braskerud and Haarstad (2003) found that the retention of linuron correlated with electrical conductivity, while metribuzin retention correlated with conductivity and TOC. We did not find any residuals of pesticides in the sediment of the wetland filter, one year after spreading in the watershed, in contrast to Daniels et al. (2000) who found that linuron and fenpropimorph could penetrate 1 m in riverbed sediments. Hence, significant release of pesticide residues from the previous year is unlikely.

**Table 3. Input of pesticides, particles, phosphorus and nitrogen to the wetland in May-October 2000 and 2001, retention in G1 and G2, total runoff and average air temperature for the corresponding time. Max pesticide concentration detected in the CW.**

	2000			2001			
	Input (g)	G1 (%)	G2 (%)	Input (g)	G1 (%)	G2 (%)	Max ( $\mu g L^{-1}$ )
fenpropimorph	4.9	24	36	5.1	2	10	1.6*
linuron	22.9	18	30	7.2	0	3	1.7*
metalaxyl	140.9	12	41	6.5	-6	-11	10
metamitron	124.4	23	58	2.8	-18	7	15*
metribuzin	28.2	22	40	0.2	15	19	2.5*
propachlor	60.0	31	67	3.5	-4	14	13*
propiconazole	11.0	16	25	13.2	5	13	2.4*
Suspended solids	$6.6 \times 10^6$	26	46	$10. \times 10^6$	16	40	
Total-P	20744	15	26	22691	14	23	
Total-N	238328	-3	8	282105	2	15	
Runoff ( $m^3$ )	48088			37394			
Air temp. ( $^{\circ}C$ )	12.5			12.8			

\* peak concentration exceeded the MAL value (conf. Table 1).

### Effect of CW size:

Doubling the surface area from G1 to G2 increased the retention for all 7 pesticides, except metalaxyl in 2001 (Table 3). For three pesticides, the increase more than doubled the retention. For the others it increased approx. 1.8 times. A similar

response was observed for phosphorus and suspended solids. Nitrogen had, however, the largest effect of increased surface area. This could be due to increased contact between microorganisms and nitrogen as the hydraulic load decreases.

#### Effect of chemical properties in pesticide:

Correlation show a retention statistically significant negative dependence only for half-life ( $T_{1/2}$ ) for both CWs. An increase in polarity index (PI) decreased the relative retention, however, it was only statistically significant for G1.

**Table 4. Correlation (r) between retention & key chemical variables in CWs G1 & G2, in 2000 (conf. Table 1 & 3).**

	Koc	$T_{1/2}$	Wat.sol.	PI	Ret. G1	Ret. G2
Koc	1					
$T_{1/2}$	0.54	1				
Water solub.	-0.2	0,37	1			
PI	0.1	0.68	0.85#	1		
Retention G1	-0.23	-0.82*	-0.57	-0.87*	1	
Retention G2	-0.68	-0.79*	0.10	-0.35	0.70	1

*statistically significant,  $P < 0.05$ . # No Normal-distribution.*

Effect of runoff intensity: In a multiple statistical analysis Braskerud and Haarstad (2003) found a positive effect on retention of linuron, fenpropimorph and metribuzin as runoff increased. This is probably an effect of increased erosion and transport of large soil particles which settle in the CW, which also has been observed for phosphorus (Braskerud, 2002).

## CONCLUSIONS

Only a few percent of the applied pesticides were leached from the watershed, still they produced concentration peaks that can be harmful for aquatic life. The relatively small CW in this study lowered the peaks, and the total amount of pesticide in the stream significantly. The relative retention increased with the CW-surface area. Chemical properties of the pesticides can indicate the potential loss from the watershed, and the retention in the wetland. Only half-life did, however, give a statistically significant estimate of the pesticide retention in CWs, even though the polarity index was also a good candidate.

## ACKNOWLEDGEMENTS

We would like to thank the Research Council of Norway (approval no. 136484/110), the Norwegian Agricultural Authority, and the County Department of Agriculture in Rogaland for their financial support. We are especially grateful to T. Kverneland for practical fieldwork, H. French for improving the English translation, and to the staffs at the Norwegian Crop Research Institute (Pesticide Laboratory) and Jordforsk LAB.

## REFERENCES

- ARSUSDA. The pesticide List. <http://wizard.arsusda.gov/acsl/ppdb3.html>
- Braskerud, B.C., 2001. Sedimentation in Small Constructed Wetlands. Retention of Particles, Phosphorus and Nitrogen in Streams from Arable Watersheds. Dr.Scient. Theses 2001:10, Agricultural University of Norway, Ås, Norway.
- Braskerud, B.C., 2002. Factors Affecting Phosphorus Retention in Small Constructed Wetlands Treating Agricultural Non-Point Source Pollution. *Ecological Engineering*, 19 (1): 41-61.
- Braskerud, B.C. and K. Haarstad, 2003. Screening the retention of 13 pesticides in a small constructed wetland treating arable stormwater runoff. *Wat. Sci. & Tech*, in press.
- Chemfinder.cambridessoft.com
- Conn, J.S., Koskinen, W.C., Werdin, N.R., Graham, J.S. 1996. Persistence of metribuzin and metabolites in two subarctic soils. *J. of Env. Qual.*, 25, 5, 1048-1053.
- Daniels, W.M., House, W.A., Rae, J.E., Parker, A. 2000. The distribution of micro-organic contaminants in river bed-sediment cores. *Science of the Total Env.*, 253, 1, 81-92.
- Holen, B. and A. Christiansen, 2001. Handbook of analytical methods for pesticide residues. The Norwegian Crop Research Institute. Ås, Norway.
- Kookana, R.S., Di, H.J., Aylmore, L.A.G. 1995. A field study of leaching and degradation of 9 pesticides in a sandy soil. *Australian J. of Soil Reseach*, 33, 6, 1019-1030.
- Ludvigsen, G., Lode, O. 2001. Results from "JOVÅ" the Agricultural and Environmental Monitoring Program of Pesticides in Norway. *Fresenius Environmental Bulletin* 10 (5), 470-474.
- Spliid, N.H. 2001. The analysis and fate of the fungicide fenpropimorph and its degradation product fenpropimorph acid in soil liquid chromatography mass spectrometry. *Int. J. of Env. Analytical Chem.*, 79, 1, 53-64.
- Tomlin, C. 1994. The pesticide manual. 10<sup>th</sup> Edition. Crop Protection Publications, 49 Downing Street, Farnham, Surrey GU9 7PH UK, 1341 pp.
- Torrents, A., Jayasundera, S., Schmidt, W.J. 1997. Influence of the polarity of organic matter on the sorption of acetamide pesticides. *J. of Agricultural and Food Chemistry*, 45, 8, 3320-3325.