ABSTRACT
Vegetative buffer zones adjacent to watercourses can be effective filters for diffuse pollution from agriculture. Several investigations, even during snowmelt season, have shown that retention of sediments and sediment-bound nutrients in runoff water has been high through buffer zones (BZ). It is likely that BZ also can be effective filters for sediment-bound pesticides. The retention of glyphosate, propiconazole, fenpropimorph and soil particles was studied in surface runoff experiments with 5-m wide buffer zones. Volume proportional samples were collected after each runoff episode (1999-2002). The distribution coefficient (Kd) shows moderate to high adsorption of the pesticides to the experimental soil. Results show average retention efficiency of about 74%, 61%, 85% and 34% for particles, glyphosate, propiconazole and fenpropimorph, respectively. The amount of AMPA (which is a degradation product of glyphosate), entering the BZ was high; approximately the same amount as glyphosate. The retention efficiency through the BZ for AMPA was about 78%. There were no significant differences in removal efficiency (in %) between winter with snowmelt and summer. This is possibly due to detachment of coarser aggregates during winter, which trap more easily in the BZ. The conclusion based on this study suggests BZ to be contributors to reduced pesticide input to surface waters.

Keywords Buffer zone; retention; glyphosate; propiconazole; fenpropimorph; soil particles

INTRODUCTION
There has been a growing concern by Norwegian authorities for risk of pesticide pollution to surface waters due to increased use of pesticides in agriculture during the last decades. According to the Plan of Action for pesticide reduction 1998-2002, one suggested method to minimise pesticide transport to surface waters, is the establishment of vegetative buffer zones (BZ) between agricultural land and surface waters (Ministry of Agriculture, 1998). Several investigations have shown that BZ can filter diffuse nutrient pollution from agriculture (e.g. Dillaha et al., 1989; Vought et al., 1994; Uusi-Kämppä et al., 2000; Syversen, 2002a). Trapping of sediments or sediment-bound nutrients is a significant retention process in BZ where surface runoff is the main transport pathway (Syversen, 2002b). However, there is a lack of knowledge regarding BZ and their effect on pesticides (Correll, 1997). Pesticides adsorbed to soil particles will probably also be trapped through surface runoff BZ. The distribution coefficient (Kd-value) expresses the ratio between the content of pesticide adsorbed to soil and the mass concentration of pesticide in the aqueous solution (Greve et al., 1998). Herbicides like glyphosate and fungicides like fenpropimorph and propiconazole have moderate to high Kd-values (Greve et al., 1998; Roy et al. 2000; Roseth and Haarstad, 2002) and low mobility in soil. However, these pesticides have been detected in watercourses in Norway (Ludvigsen and Lode, 1999), possibly transported by particles.

Adsorption, mobility and degradation of pesticides is influenced by climate and soil conditions. Low temperature and high water content in soil may for instance reduce the degradation rates for pesticides (Vink and van der Zee, 1996). In a cold climate, pesticides may therefore be detected in watercourses one year after the last application (Ludvigsen et al., in press). Norway has a "cold temperate climate", where the coldest month has a mean temperature below -3°C and the warmest month a mean above 10°C (Köppen-Geiger-Pohl classification, described by Strahler and Strahler, 1992). The surface runoff and erosion are reported to be highest during winter, especially during snowmelt periods (Lundekvam and Skøien, 1998; Øygarden, 2000). According to Syversen (2002b) BZ also had high retention of sediments and sediment-bound nutrients during winter. Higher surface runoff and erosion during winter caused erosion of coarser particles, which trapped more easily in the BZ. This paper will examine whether particle-bound pesticides also have high retention in surface runoff BZ during winter.

The objectives of this paper are to 1) quantify the reduction of particle-bound pesticides (glyphosate, fenpropimorph and propiconazole) in surface runoff buffer zones, and 2) document the function of these BZ on glyphosate, fenpropimorph and propiconazole reduction during winter compared to summer.

METHODS
Field site descriptions
The experimental site was established in 1999 in the southeastern part of Norway (60° N), about 70 km northeast of Oslo. Four study plots with an upper supply area of 10 m x 45 m each with cereal production (barley), and a lower part with a buffer zone area of 10 m x 5 m (two plots) and no buffer zone (two reference plots) (Fig. 1), respectively, were used. The upper area was tilled (harrowed) in the winter. The application time for fenpropimorph and propiconazole was summer (July 2000) and autumn (September 1999) for glyphosate. The application rate represented a normal pesticide application in the area, which was 3000 ml Round UpEco/ha (active pesticide: glyphosate-360 g/L ) and 1000 ml TiltTop/ha (active
pesticides: fenpropimorph-375 g/L and propiconazole -125 g/L). The slope of the experimental site was 14% and the soil type was levelled silty clay loam with 45% clay, 52% silt, 3% sand, and 1.5% organic matter. The dominant plant species of the BZ were thistle \textit{Circium arvense} (L.) Scop., common couch \textit{Elytrigia repens repens} (L.) Desv. Ex Nevski, timothy \textit{Phleum pratense pratense} L., tufted hair grass \textit{Deschàpsia cespitòsa cespitòsa} (L.) Beauv and meadow fescue \textit{Festuca pratensis} Huds.

Figure 1 Horizontal view of the experimental site including plot with no BZ (reference plot) and 5-m wide BZ. Measuring stat. = measuring stations. The supply area has cereal production (barley) during summer and is tilled (harrowed) during winter.

Water samples
Surface runoff water from the plots was led through inlet pipes to measuring stations with a tipping bucket system equipped with a mechanical counter and a datalogger. The datalogger registered the tipping number, and discharges were calculated. For every second full bucket a portion of water was led to a sampling tank. Volume proportional mixed samples were taken after every runoff event or as frequently as 1-2 times a day during the snowmelt period. From the sampling tank, water samples were collected for laboratory analysis of glyphosate, fenpropimorph, propiconazole, suspended solids (SS), and soil texture.

Glyphosate and AMPA (aminomethylphosphonic acid) analysis were carried out in acidified (pH 2) water samples, and stored at 4 °C. AMPA is a degradation product of glyphosate. Only the supernatant from the samples was prepared for analysis. The samples were concentrated in two ion exchangers, derivatised twice and analysed by gas chromatography with mass-spectrometric detection (GC/MS-SIM). The detection limit was 0.01 ìg/L. For fenpropimorph and propiconazole the samples were analysed by gas chromatography (GC-MULTI M03) (for more details, see Holen et al., 2002). Suspended solids were analysed according to Norwegian Standard 4733. Soil texture was analysed by filtering the water sample through a 0.45 µm Millipore filter. Aggregates were dispersed in an ultrasonic bath, before being injected to a Coulter LS 230 laser. The laser diffraction texture analysis is a technique that measures the light scatter from an ensemble of particles. Compared to traditional methods, the laser diffraction technique gives high resolution curves (for more details, see Syversen and Borch, 2002). Textural classes are displayed in Table 1.

<table>
<thead>
<tr>
<th>Table 1 Textural classes for particle sizes analysis.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clay</td>
</tr>
<tr>
<td>------</td>
</tr>
<tr>
<td>Fine</td>
</tr>
<tr>
<td>0.06-0.2 ìm</td>
</tr>
</tbody>
</table>
Effects of soil particles on recovery of glyphosate

Because only the supernatant was analysed for glyphosate, a separate experiment was designed in order to investigate the recovery of total amount of glyphosate as a function of level of suspended solids (SS), particle size of SS in the water samples, and application rate of glyphosate. Recovery was calculated as the sum of measured glyphosate and AMPA divided by glyphosate added in the experiment. Differences in molecular weight between glyphosate and AMPA were corrected for. The dataanalyses showed no statistically significant effect of different levels of glyphosate and clay content on the recovery of glyphosate. The effect of SS was significant for glyphosate (for more details, see Syversen and Bechmann, in press). The recovery of glyphosate (%) in water samples (R) was calculated as follows:

\[ R = -9.64 \ln(\text{SS}) + 113 \]  

(1)

Glyphosate results presented later in this paper were adjusted according to this relationship and also corrected for recovery of the analysis itself, which was 87 %.

Recovery of fenpropimorph and propiconazole

Standards with known concentration of fenpropimorph and propiconazole were analysed simultaneously with the water samples. The recovery of fenpropimorph varied from 73-124%, with an average of 95% (n=11), while the recovery of propiconazole varied from 98-181%, with an average of 121 % (n=21). Corrections for recovery of fenpropimorph and propiconazole were made.

Calculations of retention through the buffer zone

Due to equal area, soil type and slope, the runoff from the reference plots was expected to be similar to runoff into the BZ plots. However, differences in runoff between these plots were measured. To correct for the differences in input to the BZ, runoff from these four plots was compared from 1992-1993. A simple linear regression model was used to correct for differences in runoff between the plots. The corrections were made after the following equation:

\[ Q_{\text{in}} = 396.43 + 0.76 \times Q_{\text{ref}} \]  

(2)

where \( Q_{\text{in}} \) is the average surface runoff (L) into the 5-m wide BZ and the \( Q_{\text{ref}} \) is the average surface runoff for the reference plots, both summed over a runoff event.

Accumulated runoff over the correction period from plot 1 and 2 (input to the 5-m BZ) was 65% of the reference plots (plot 3 and 4). The input (In) and output (Out) of pesticide and particle loads were calculated by multiplying pesticide and particle concentrations (C) and surface runoff (Q), summed over a runoff event. Results from the reference plot (average of plot 3 and 4) were used as an input value, while the output value was determined after passing the 5 m wide BZ (average of plot 1 and 2) (Fig. 1). The removal efficiency in % (Rem) through the BZ was calculated according to:

\[ \text{Rem} = \left( \frac{Q_{\text{in}} C_{\text{in}} - Q_{\text{out}} C_{\text{out}}}{Q_{\text{in}} C_{\text{in}}} \right) \times 100 \]  

(3)

In a few cases, the calculated values for \( Q_{\text{in}} \) was less than the measured values for \( Q_{\text{out}} \). In these cases we made the assumptions that \( Q_{\text{in}} = Q_{\text{out}} \).

RESULTS AND DISCUSSION

Climate and hydrology

Table 2 shows the monthly average temperatures during the study period compared to the normal period 1961-90. The data are measured at a meteorological station situated close to the study site. Every year in the study period fits into the definition of “cold temperate climate”.

<table>
<thead>
<tr>
<th>Temperature (ºC)</th>
<th>Jan</th>
<th>Feb</th>
<th>Mar</th>
<th>Apr</th>
<th>May</th>
<th>Jun</th>
<th>Jul</th>
<th>Aug</th>
<th>Sep</th>
<th>Oct</th>
<th>Nov</th>
<th>Dec</th>
<th>Yr.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1999-2002</td>
<td>-4.5</td>
<td>-5.3</td>
<td>-1.0</td>
<td>4.3</td>
<td>11.1</td>
<td>13.5</td>
<td>15.6</td>
<td>14.1</td>
<td>10.9</td>
<td>7.0</td>
<td>2.5</td>
<td>-4.4</td>
<td>5.3</td>
</tr>
<tr>
<td>Normal 1961-90</td>
<td>-6.9</td>
<td>-6.8</td>
<td>-1.8</td>
<td>3.2</td>
<td>9.7</td>
<td>14.1</td>
<td>15.0</td>
<td>14.0</td>
<td>9.5</td>
<td>5.1</td>
<td>-1.4</td>
<td>-5.3</td>
<td>4.0</td>
</tr>
</tbody>
</table>

The winter period is in this paper defined from the first snowfall (usually early November) to the end of the snowmelt period (in April). The winter period is mainly characterised by frozen soil, freezing and thawing cycles, and high surface runoff during snowmelt events. Over 80% of the total surface runoff occurs during winter, while the precipitation during the same period is 28% (Figure 2). In another similar study area with BZ (Syversen, 2002b), the same figure for surface runoff was over 90%, while the precipitation was 43% of total precipitation during the study period (1992-99). Higher surface runoff and precipitation during summertime in the present study compared to Syversen (2002b) is mainly due to very high precipitation and high runoff during the summer period 2000 (Figure 2). About half of the precipitation for the whole year occurred in 2.5-months during the autumn of 2000. Due to much higher infiltration rate and evapotranspiration
during summertime, only 5% of the precipitation results in surface runoff during summer while about 56% of the precipitation results in surface runoff during winter. It was expected that surface runoff during winter was almost the same or slightly less than precipitation because of restricted infiltration, no uptake of water into the vegetation, and less evapotranspiration. As shown in figure 2, the winter periods have less surface runoff than expected compared to the precipitation in the same period. This can be due to infiltration of surface water into the soil under conditions with partly frozen soil. According to Kok and McCool (1990) and Burn (1991), infiltration has been documented to occur even if the soil is frozen. The water saturation of the soil at the time of freezing the previous autumn is of significant importance.

![Figure 2 Runoff and precipitation in mm during winter (W) and summer (S), 1999-2002. The winter is defined as the period from the first of November (or the nearest snowfall) to the end of snowmelt.](image)

**Removal efficiency of pesticides**

Average removal efficiency during the experimental period is quite high; 51%, 48%, 85% and 34% for particles, glyphosate, propiconazole and fenpropimorph, respectively. The experimental period differs, however, for the parameters (Fig. 3). The removal efficiency for AMPA is 67% during the experimental period. Glyphosate has a high affinity to soil, especially to clay particles (Greve et al., 1996). The distribution coefficient of the experimental soil for glyphosate ($K_d$-value) varied from 461-1539 mL/g soil (Syversen et al., 2000; Thorstensen and Linjordet, in preparation). The high $K_d$-value may explain why the removal efficiency of glyphosate and AMPA follows the removal efficiency of particles. Glyphosate and AMPA are trapped in the BZ, because they are adsorbed to soil particles. Sedimentation of soil particles is an essential retention process in surface runoff buffer zones (Haan et al., 1994; Syversen, 2002a). There is a positive significant correlation (P<0.05) between particles (SS) and glyphosate both in inlet and outlet water from the buffer zone.

A study conducted by Syversen and Bechmann (2003) with BZ with simulated surface runoff, showed a removal efficiency of 39% for glyphosate. Lower removal efficiency of glyphosate was probably caused by adsorption to the fine and medium silt fraction. The fine silt fraction did not trap effectively in the BZ. According to a review article by Baker et al. (1995) BZ reduce herbicide runoff by up to 90%. Glyphosate was not a part of the review. They concluded that the efficiency of the herbicide removal in the BZ was a function of soil moisture, runoff volume and herbicide concentration. The $K_d$-value for propiconazole and fenpropimorph was 11-22 and 12-17 mL/g soil, respectively, which is characterised as moderate adsorption to soil (Syversen et al., 2000; Thorstensen and Linjordet, in preparation). Lower adsorption affinity for fenpropimorph to soil may explain lower removal efficiency. The removal efficiency of propiconazole, however, is very high. Although there is a weak positive correlation between particles and propiconazole, the regression coefficient is very small and not significant (P>0.05). Figure 3 shows runoff events in the beginning of the snowmelt period in 2000 with high retention of particles, glyphosate and AMPA. The experiment with propiconazole and fenpropimorph had not started at this point. This runoff event accounts for 30-40% of all retention for the whole experimental period for glyphosate and AMPA, while the same figure for particles is about 40%. If we compare the removal efficiency for particles, glyphosate and AMPA over the same experimental period as for propiconazole and fenpropimorph, the efficiency then becomes 35, 36 and 55%, respectively. This illustrates the importance of event-based monitoring strategy.
Figure 3  Retention of particles (suspended solids, kg), glyphosate, AMPA, propiconazole and fenpropimorph (mg) in the buffer zone during the experimental period.

Seasonal variation in removal efficiency
The major surface runoff occurs during wintertime. It is therefore essential to document the removal efficiency during this period. Figure 4 shows the average removal efficiency (%) during winter and summer for particles, glyphosate, AMPA, propiconazole and fenpropimorph. It was expected that BZ were more effective during summer due to higher vegetation density and therefore higher trapping efficiency of particles and particle-bound pesticides, higher degradation rate of pesticides due to higher temperature, uptake of pesticides into the vegetation, and lower surface runoff intensity. There were, however, no significant differences in removal efficiency (%) between winter and summer for any of the parameters (P>0.05). This result is in accordance with results from a similar BZ experiment (Syversen, 2000b; Syversen and Borch, 2002), where no significant differences in removal efficiency between summer and winter for particles and particle-bound nutrients were documented. A higher portion of silt and sand in runoff water during winter runoff events compared to summer runoff events were reported. Higher runoff velocity during winter may cause detachment of coarser particles. Coarser particles trap more easily in the BZ. However, this was not the case in the present experiment. In the present study there were no significant differences in silt and sand fraction in runoff water between summer and winter. The soil texture, however, was quite different in the present study compared to Syversen (2002b) and Syversen and Borch (2002). The content of clay was about 45% in the present study, over twice as much as in Syversen (2002b)/Syversen and Borch (2002). There was a significantly higher content of fine clay in the present study in runoff water during winter compared to summer. Fine clay may have been transported as aggregates, and therefore trapped in the BZ. Also Syversen and Borch (2002) reported that clay particles possibly are trapped as aggregates in BZ. Another difference between these two experiments is that summer runoff is much higher in the present study. This will also lead to less difference between size of particles detached during winter compared to summer. There was significantly lower relative content of silt and sand in runoff after passing the BZ than into the BZ in the present study, indicating that the silt and sand fraction was trapped in the BZ.
CONCLUSIONS

In this experiment, carried out in a "cold temperate climate" in the Southern part of Norway, over 80% of the total surface runoff occurred during winter, while the same figure for precipitation was 28%. About 56% of the precipitation lead to surface runoff during winter, while only 5% of the precipitation caused surface runoff during summer. Average removal efficiency for the experimental period was 51%, 48%, 85% and 34% for particles, glyphosate, propiconazole and fenpropimorph, respectively. Glyphosate had a high affinity to the experimental soil while the affinity of propiconazole and fenpropimorph was moderate. Runoff events in the beginning of the snowmelt of 2000 accounted for 30-40% of all retention during the whole experimental period for glyphosate and AMPA, while the same figure for particles was about 40%. This illustrates the significance of event-based sampling strategy. There were no significant differences in removal efficiency (in %) between winter and summer for any of the parameters studied, but higher total retention (in g) during winter due to higher runoff. This is possibly due to detachment of coarser aggregates during winter, which trap more easily in the BZ.

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REFERENCES


