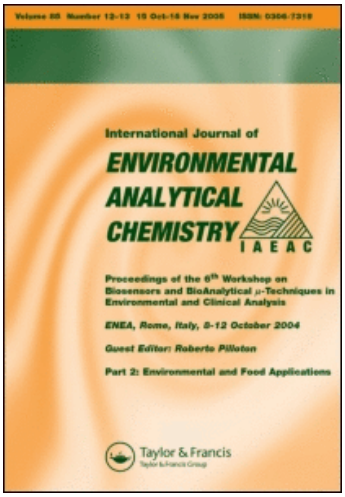

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Trends of Pesticides in Norwegian Streams and Rivers (1996-2000)

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TRENDS OF PESTICIDES IN NORWEGIAN STREAMS AND RIVERS (1996–2000)

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In Norway twelve streams and medium size rivers have been monitored for pesticides in a four to six years period. During these years the central authorities have accomplished efforts to minimize the risk for pesticides entering the water bodies. Trend analyses have been done on the years 1996–2000 to gain information on whether there have been reductions in the retrieval of the pesticides: (1) Frequency of pesticides detection; (2) Sum concentration of all individual pesticides in each sample; (3) Environmental risk by weighing the concentration of each pesticide against the environmental maximum residue limits (MRL). As a whole, developments in streams and rivers show both positive and negative trends regarding the different parameters studied. The tendency is that the different parameters show the same development within the stream.

The situation in these streams has not changed much during this 5 years period, but there are indications towards a slight positive development. Trend analyses might therefore be useful together with careful interpretation.

Keywords: Pesticides; Monitoring; Streams; Rivers; Trend-analyses

INTRODUCTION

Considerable effort has been done all over the world the last two decades to monitor for contamination by pesticides in streams and rivers, and a number of compounds have been detected [1–3]. In Norway a monitoring program started in 1995 by the Ministry of Agriculture, in co-operation with the Ministry of Environment. The primary objectives for the program were: (1) To gain information on the occurrence of pesticides in water and potential risks of water contamination; (2) To clarify the connection between the use of pesticides on farmland and their occurrence in water as a tool to evaluate if the authorisations of the pesticides give the wanted effects; (3) To demonstrate possible changes in the use of pesticides by the farmers within the agricultural industry.

The central authorities have accomplished efforts to minimise the risk for pesticides entering the water bodies. Some pesticides have been withdrawn and other pesticides

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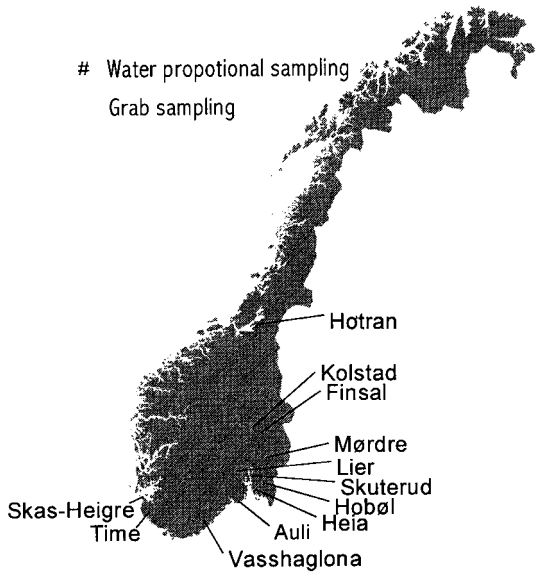

FIGURE 1 Map of Norway showing the monitored streams and rivers.

have been given approval and introduced on the marked. Mostly all farmers in Norway have completed a course on pesticide management and campaigns with information on risks have been carried out. It is therefore important to evaluate whether there have been any changes in retrieval of the pesticides in the streams. Twelve out of sixteen streams and rivers have been monitored for pesticides in a four to six year period and are analysed to observe trends (Fig. 1).

The locations monitored represent different agricultural farming practices, natural resource bases, and various agro-climatological conditions [4]. The investigations give therefore an "overall picture" on developments of different cropping systems. The major issue of this article is therefore to present the methods to analyse trends. The interpretation of the results must be done regarding the limitations of the investigations of the monitoring program with dynamic factors.

EXPERIMENTAL

Runoff Measurement

The basis for the monitoring programme is six rather small catchments that have continuous discharge measurements and water proportional samplings monitored 1995 till 2000. The catchments vary in size from 50 to 680 hectares and the total number of farms varies from 5 to 30. The farmers keep records of all their farming operations including pesticides use and run their farms without any particular consultation or restrictions on farming practices [4]. Pesticides have been monitored for four years or more at additional six small and medium size rivers. The catchments size vary from 20 till 230 km^2. Samples have been collected as grab samples (Table I).

Samples are taken regularly from the month March or April (when the snow melts) to the end of December when frost appears. Some samples have also been taken during

TABLE I Characteristics of the catchments in the monitored streams and rivers

Location	*Drainage area* (km^2)	*Main crop*	*Soil type*	*Mean precipitation* ($mm\,year^{-1}$)
Vasshaglona	0,7	Vegetables, potatoes and grain	Sand and loam	1230
Time	1,1	Grass	Soils of morenic origin with loamy sand	1189
Kolstad	3,1	Grain	Soils of morenic origin with loam soil	585
Skuterud	4,5	Grain	Silty clay, shore deposit and morenic depositions	785
Heia	4,7	Vegetables, potatoes and grain,	Sand, silt and clay of morenic origin	829
Mørdre	6,8	Grain	Clay and silt fractions of marine and lacustrine origin	665
Hotran	20	Grain and 30% grass	Silt loam and silt clay loam of marine origin	892
Finsal	22	Grain and potatoes	Soils of morenic origin	585
Skas–Heigre	29	Grass	Clay, sand and gravel	1180
Auli	147	Grain	Clay of marine and morenic origin	1035
Lier	303	Vegetables, grain	Clay and silt fractions of marine and fluvial origin	940
Hobøl	331	Grain	Clay and silt fractions of marine origin	829

the winter months, especially the years when it has not been permanent frost in the soil. In some locations the termination of the sampling seasons have been in October/November. Therefore, the number of samples taken every year vary between the locations. Within a location the number of samples taken every year are rather stable. The information on the pesticide used in the catchments is collected every year.

Chemical Analyses

Determination of pesticides residues in water is mainly performed by gas chromatography with selective detectors after extraction with organic solvents – GC multimethod. In addition, some of the more polar herbicides like the phenoxy-acids require a derivatisation step before the chromatographic analysis – GC/MS multimethod. All three groups of compounds, herbicides, insecticides and fungicides are represented. The compounds most commonly used are included. The number of substances analysed and the detection limits have been improved during the monitoring period. In 1996 only 30 substances where analysed and every year the number of pesticides analysed have increased, ending up with 48 pesticides analysed by multimethods the year 2000. Seventeen pesticides have been added after 1996, but except for 2,6-diklorbenzamid (BAM) there are relatively few detections of the newcomers (Table II). There have been very few changes in detection limits for each pesticide. The results can therefore be interpreted overlooking this problem.

Additional analyses have been done on important substances that require special analysing methods such as glyphosate, tribuneron-metyl, ETU (decomposition product of mancozeb) and isoproturon. The number of pesticides analysed vary (Table III).

Because there have been changes both in the market on what pesticide to be preferred and of the doses used, the trend analyses are done on the total of pesticide detected.

TABLE II Pesticides analysed by multi-methods by the Norwegian Crop Research Institute, pesticide laboratory, sorted on the number analysed and detected

Pesticide	*Group*	*Number analysed 1996–2000*	*Number detected*	*Limits of termination* (μg/L)	*Uncertainty* (%)	*MRL* (μg/L)
Bentazone	Herbicide	845	344	0.02	44	540
Metribuzine	Herbicide	845	189	0.05	62	2.2
MCPA	Herbicide	845	185	0.02	23	740
Dichlorprop	Herbicide	845	139	0.02	32	71
Metalaxyl	Fungicide	845	110	0.1	49	280
Mecoprop	Herbicide	845	104	0.02	19	510
Linuron	Herbicide	845	72	0.1	36	0.7
Simazine	Herbicide	845	56	0.05	36	4.2
2,4-D	Herbicide	845	49	0.02	28	14
Propachlor	Herbicide	845	39	0.1	54	2.9
Metamitron	Herbicide	845	38	0.1	64	11
Lindane	Insecticide	845	33	0.05	36	1.6
Propiconazole	Fungicide	845	27	0.1	31	0.02
Chlorfenvinphos	Insecticide	845	22	0.1	30	0.043
Aclonifen	Herbicide	845	9	0.05	31	0.67
Dimethoate	Insecticide	845	7	0.05	24	0.2
Azinphosmethyl	Insecticide	845	4	0.1	31	0.01
Thiabendazole	Fungicide	845	3	0.1	34	2.8
Prochloraz	Fungicide	845	3	0.1	43	4.6
Pirimicarb	Insecticide	845	3	0.1	60	0.14
Terbutylazine	Herbicide	845	1	0.1	40	1.6
Vinklozolin	Fungicide	845	0	0.05	49	40
Permethrin	Insecticide	845	0	0.1	34	0.025
Fenvalerate	Insecticide	845	0	0.1	27	0.036
Fenitrothion	Insecticide	845	0	0.05	45	0.086
Endosulfan-alpha	Insecticide	$\sum = 845$	0	0.1	40	0.003
Endosulfan-beta	Insecticide				36	–
Endosulfan sulfat	Metabolite				35	–
Diazinon	Insecticide	845	0	0.05	36	0.01
DDD-p,p′	Metabolite	$\sum = 845$	0	0.1	25	
DDE-p,p′	Metabolite				35	
DDT-o,p′	Insecticide				35	0.004
DDT-p,p′	Insecticide				34	–
Atrazine*	Herbicide	845	0	0.05	32	4.3
Atrazine-desethyl	Metabolite	845	0	0.05	28	–
Atrazine-desisopropyl	Metabolite	845	0	0.05	33	–
Alpha- cypermetrin	Insecticide	845	0	0.05	23	0.003
Fluroxypyr	Herbicide	688	4	0.1	53	143
Iprodione	Fungicide	688	2	0.1	30	2.5
Tebuconazole	Fungicide	688	0	0.1	20	11
Fenpropimorph	Fungicide	688	0	0.05	77	17
Dicamba	Herbicide	414	4	0.02	30	1110
Penconazole	Fungicide	414	0	0.05	35	11
Esfenvalerate	Insecticide	414	0	0.05	34	0.0005
2,6-diklorbenzamid (BAM)	Metabolite	345	28	0.05	29	38
Fluazinam	Fungicide	345	4	0.05	50	0.55
Chlorpropham	Herbicide	244	8	0.05	39	100
Chlopyralid	Herbicide	244	2	0.1	63	690
Flamprop	Herbicide	244	1	0.1	49	25
Pyrimethanil	Fungicide	244	0	0.02	33	29
Lambdacyhalotrin	Insecticide	244	0	0.05	27	0.0024
Cyprodinil	Fungicide	72	0	0.02	13	0.33
Cyprokonazol	Fungicide	72	0	0.02	44	7.7
Imazalil	Fungicide	72	0	0.1	58	120

TABLE III Pesticides analysed by special methods by Miljø Kjemi, Denmark

Pesticide	*Group*	*Number analysed 1996–2000*	*Number detected*	*Limits of termination* (μg/L)	*Uncertainty* (%)	*MRL* (μg/L)
Glyphosate	Herbicide	57	52	0.01	–	12
ETU[a]	Metabolite	30	8	0.01	40	0.26
Isoproturone[b]	Herbicide	52	8	0.01	–	0.3
Tribenuron-methyl	Herbicide	17	0	0.01	–	1
Metsulfuron-methyl	Herbicide	8	0	0.01	–	0.04
Chlorsulfuron	Herbicide	8	0	0.01	–	0.01
Thifensulfuron-metyl	Herbicide	8	0	0.01	–	0.13
Triasulfuron	Herbicide	8	0	0.01	–	0.02

[a]ETU is a decomposition product of mancozeb; [b]Analysed by Norwegian Crop Research Institute, Pesticide Laboratory.

Additional analyses have been done to excluding those pesticides that have not been monitored all years, to gain information on the influence of the expansion of the analytical spectrum. Table II illustrate the pesticides analysed and list the number of analyses of each pesticide. Limits of termination and detection uncertainty are given for the year 2000. The table also gives the environmental maximum residue limits (MRL) that are used to calculate the environmental risk.

Trend Analyses

One way of handling the results is to study separately the detection frequency and concentrations for each pesticide. This would give information only of that very pesticide and not for the total. Because we have a dynamic system that reflects the updated way of farming and the evaluation is related to the development of the streams, an integrated approach was chosen. Three different parameters were studied to evaluate trends in the retrieval of the pesticides: (1) Frequency of pesticides detection; (2) Sum concentration of all individual pesticides in each sample; (3) Environmental risk by weighing the concentration of each pesticide against the environmental MRL.

(1) The relative detection frequency was derived each month by calculating the ratio between the number of samples in which pesticides were detected and the total number of samples that month. The relative detection frequency per month was denoted by F_{ij} $i=1,2,\ldots,n$, $j=1,2,\ldots,12$ where i the year of sampling, and j the month of sampling. The relative detection frequency was seasonally adjusted according to $F(\text{adj})_{ij}=F_{ij}/F(\text{mean})_j$, where $F(\text{mean})_j$ denote the monthly mean detection frequency and calculated according to:

$$F(\text{mean})_j = \sum_{i=1}^{n} F_{ij}/n, \quad j = 1, 2, \ldots 12$$

Months with no sampling were not seasonally adjusted and regarded as missing value.

(2) The sum concentration of all individual pesticides was derived each month by calculating the ratio between the sum of concentrations of all individual pesticides and the total number of samples that month. The sum concentration per month was denoted by $C_{ij}, i = 1,2,\ldots,n$, $j = 1,2,\ldots,12$, where i the year of sampling, and j the month of sampling. The relative sum concentration was seasonally adjusted according

to $C(\text{adj})_{ij} = C_{ij}/C(\text{mean})_j$, where $C(\text{mean})_j$ denote the sum concentration of all individual pesticides and calculated according to

$$C(\text{mean})_j = \sum_{i=1}^{n} C_{ij}/n, \quad j = 1, 2, \ldots, 12$$

Months with no sampling were not seasonally adjusted and regarded as missing value.

(3) The environmental risk of pesticides in surface water was calculated using the environmental MRL of each pesticide detected. These limits are based on the EC_{50} or LD_{50} values for algae, water plants, daphnia or fishes. The most sensitive organism is used to calculate the MFL value. A safety factor of 10 has been used on the EC_{50} values for algae and water plants. A safety factor of 100 is used on the LD_{50} values on daphnia and fishes. If concentrations of a pesticide rise above the environmental maximum residue limit, there might be a potential risk for the aquatic environment. The total environmental risk index (TRI) was derived each month by establish a sum risk index of all pesticides (k) detected this month. This is done by calculating the ratio between the concentrations of each pesticide (k) divided on environmental residue limits (MRL) for that pesticide according to

$$TRI = \sum_{k=1}^{n} C_k/MRL_k, \quad \text{and} \quad TRI_{ij} \quad i = 1, 2, \ldots, n, \; j = 1, 2, \ldots, 12,$$

where i the year of sampling, and j the month of sampling. The TRI was seasonally adjusted according to $TRI(\text{adj})_{ij} = TRI_{ij}/TRI(\text{mean})_j$, where $TRI(\text{mean})_j$ denote the monthly total environmental risk index and calculated according to:

$$TRI(\text{mean})_j = \sum_{i=1}^{n} TRI_{ij}/n, \quad j = 1, 2, \ldots, 12$$

Months with no sampling were not seasonally adjusted and regarded as missing value.

The datasets have been analysed using two statistical methods; linear regression and nonparametric regression (Kendalls Tau) in order to compare the outcome.

RESULTS AND DISCUSSION

Trends in the potential for environmental risk must be interpreted recognizing the dynamic system between pesticide use and their different characteristics, changes both in the area of time and concentrations applied and commercial appearance of new pesticides and disappearance of others. Within the catchments there are different soil properties and rotations in crops. Climatic factors such as precipitation and temperature show annual variations. Changes concerning analysing methods, especially expansion of the analytical spectrum must be carefully examined.

Results from the statistical analyses must therefore be completed by an evaluation on what pesticides are used and found in each catchment area and the changes that have appeared during the last five years. The data on the pesticide use is not presented in this article, because of the space demand. However information on the major changes

of pesticide use are given in the text. Of the total, 32 pesticides of a number of 56 substances analysed were detected in surface water (Table II).

Both the linear regression and the non-parametric test showed the same results with respect to significance except for the Hotran case. A significant decrease both for frequency of detection, sum concentrations and total risk index appeared at Kolstad stream (Fig. 2). The Kolstad catchment is dominated by grain growing on moraine soil. One reasonable explanation on these results is the fact that there have been a change in the use of pesticides from phenoxy acid herbicides to low dose herbicides (sulfuron-ureas) which are not likely to be found in the relevant concentrations.

The Heia stream gather water from the most intensive farmland dominated by vegetable growing on light soils. The stream has the highest numbers of pesticides detected. Figure 3 show a significant reduction for the parameter frequency of detection and total risk index. The sum concentration is not significant but tend towards a reduction. In this area there have been a focus on the pesticide residues since 1997, and a special campaign was started in 1999 focusing on what pesticide to use. The farmers records show reductions in the doses of metribuzine and linuron applied. These pesticides gave the best contribution to the total risk index.

Hotran stream showed a significant reduction of sum concentration and total risk index, while the two statistical methods show differences for the adjusted frequency. Here the non-parametric test is prefered giving no significance. Data on pesticide use is not available in this catchment and interpretation of the tests is therefore more uncertain (Fig. 4).

A significant increase both for frequency of detection and sum of concentrations appeared at two locations: Vasshaglona catchment (Fig. 5) is dominated by vegetables, potatoes and grain (sandy soil) and Skuterud catchment (Fig. 6) is growing grain (clay soil). Additional analyses are done on these two locations excluding those pesticides that have not been monitored all years. Then, no significant increase in the studied parameters of the Skuterud stream was found. Indicating that the expansion of the analytical spectrum might be the major factor for the increase in the pesticide detection. The farmers registration books support this conclusion and show no general increase in the use of pesticide. The same analyses were done on the Vasshaglona stream. Significant increase was found for all three parameters investigated. On this location we can therefore conclude that the increase is not related to the expansion of the analytical spectrum. The farmers books give no clear explanations on these increase.

We conclude that development in streams and rivers show both positive and negative trends regarding different parameters studied. The tendency is that the different parameters; frequency of pesticide detection, sum of concentrations and total risk index show the same development within the stream studied. When using the ''bulk'' of pesticides detected, the method does not handle the problem associated with the expansion of the analytical spectrum. Studying only those pesticides that have been analysed all years, give additional information about the influence of the analytical spectrum. To handle the fact that pesticides are taken off the marked, new once are introduced, doses are chanced and so on a more careful interpretation of the developments for the individual pesticide is needed.

However, the analyses give a broad outline, that might be interpreted to conclude that the situation in these streams has not changed much during this 5 years period, but there are indications towards a slight positive development. Trend analyses might therefore be useful together with careful interpretation.

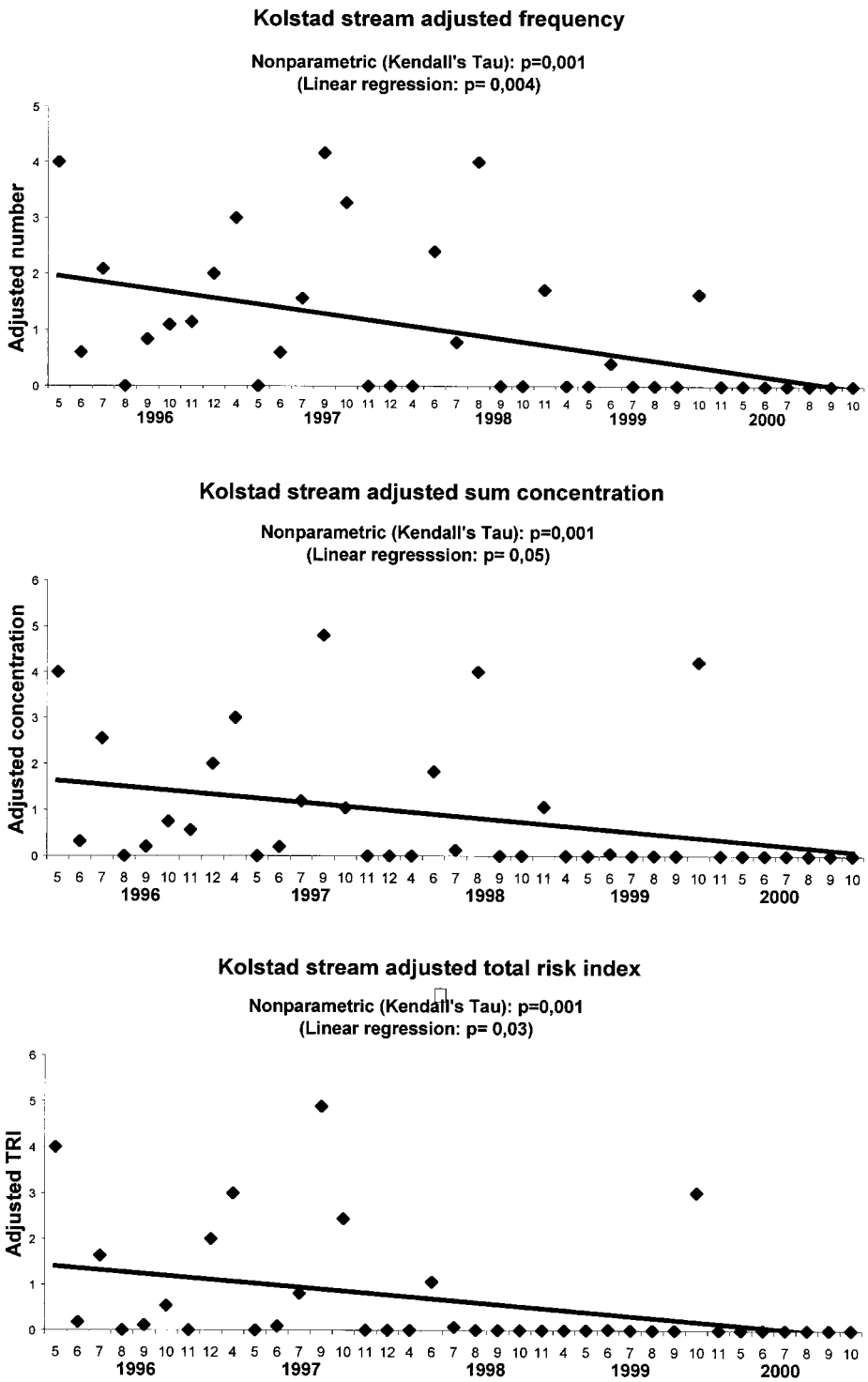

FIGURE 2 Results from trend analyses in Kolstad stream.

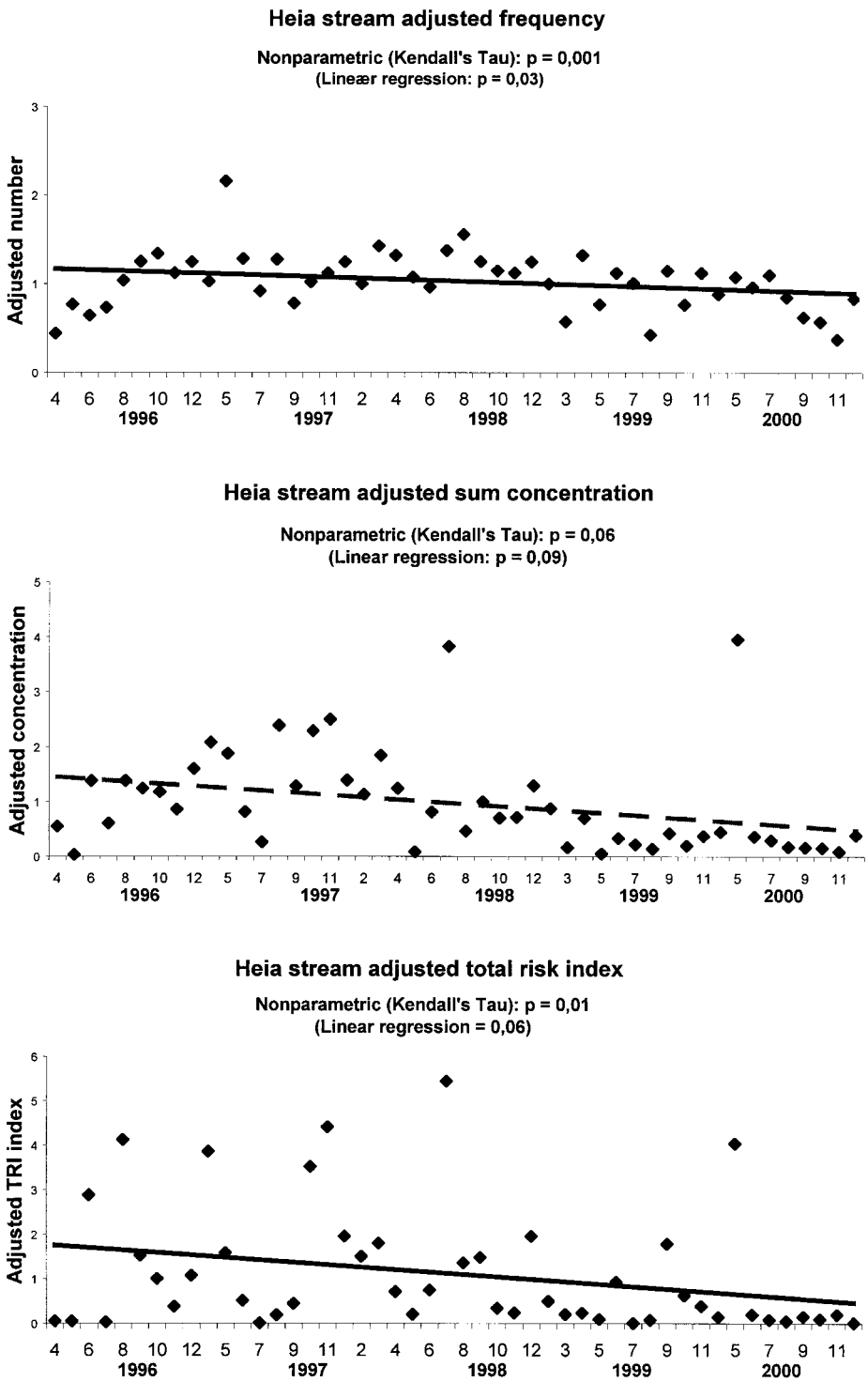

FIGURE 3 Results from trend analyses in Heia stream.

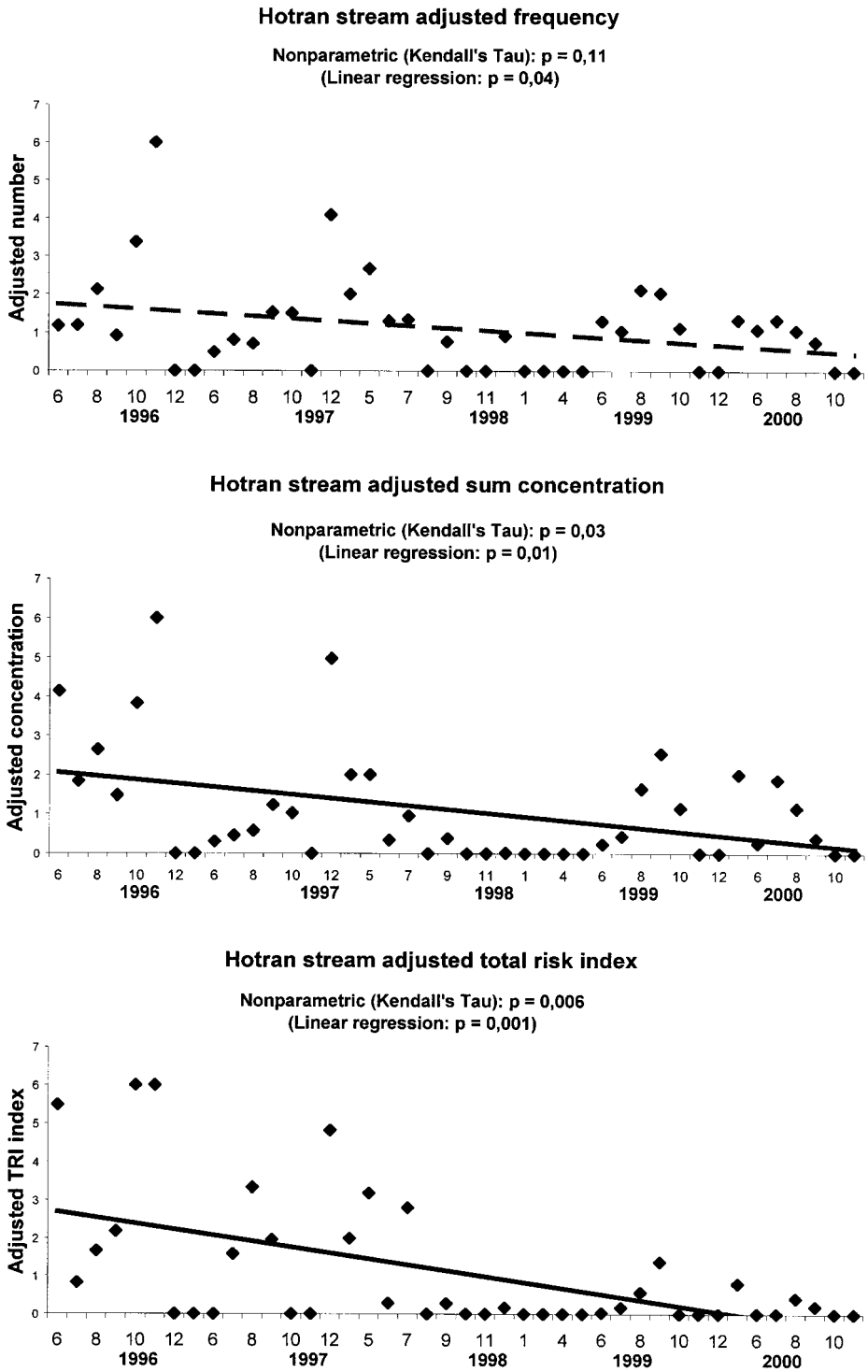

FIGURE 4 Results from trend analyses in Hotran stream.

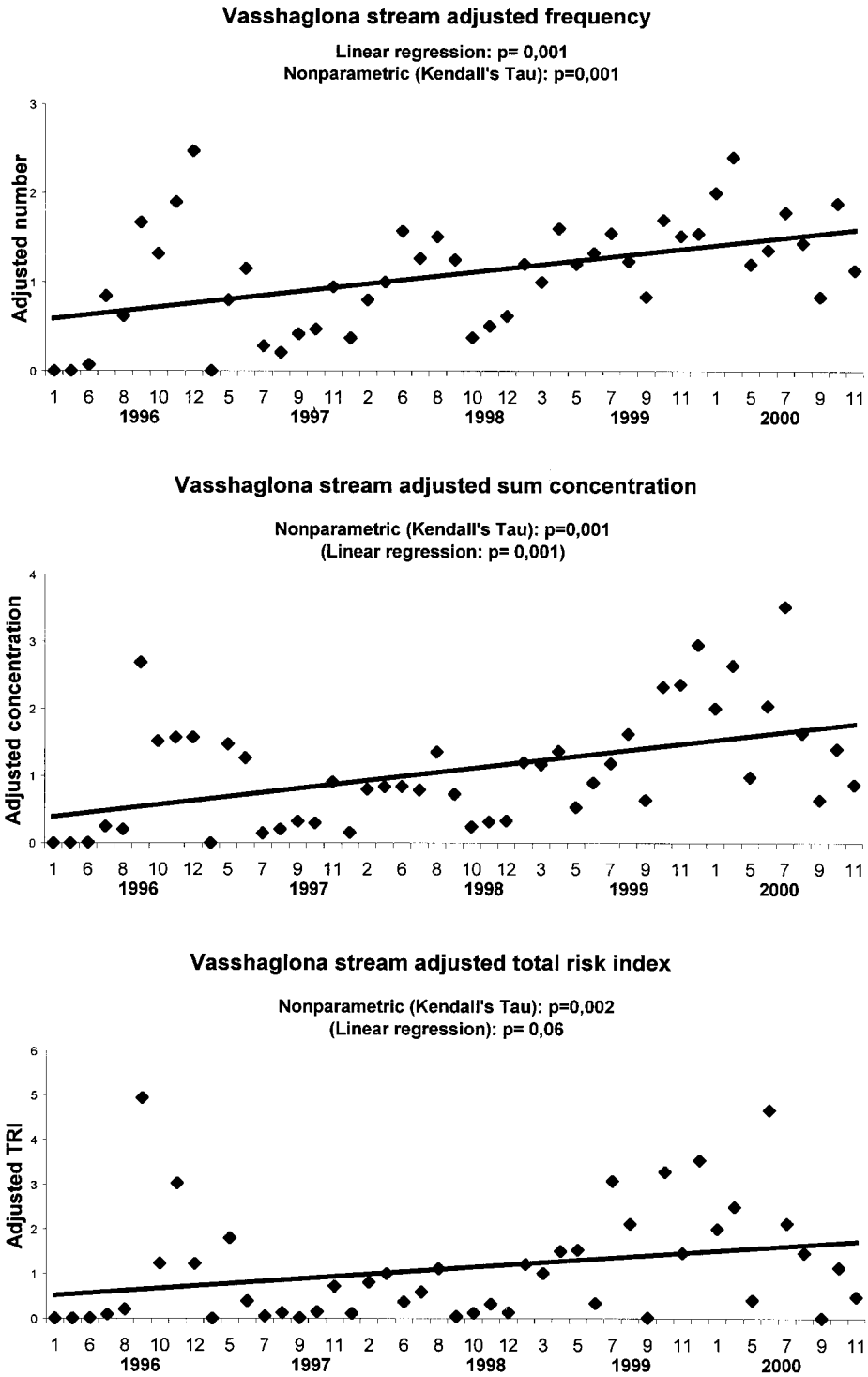

FIGURE 5 Results from trend analyses in Vasshaglona stream.

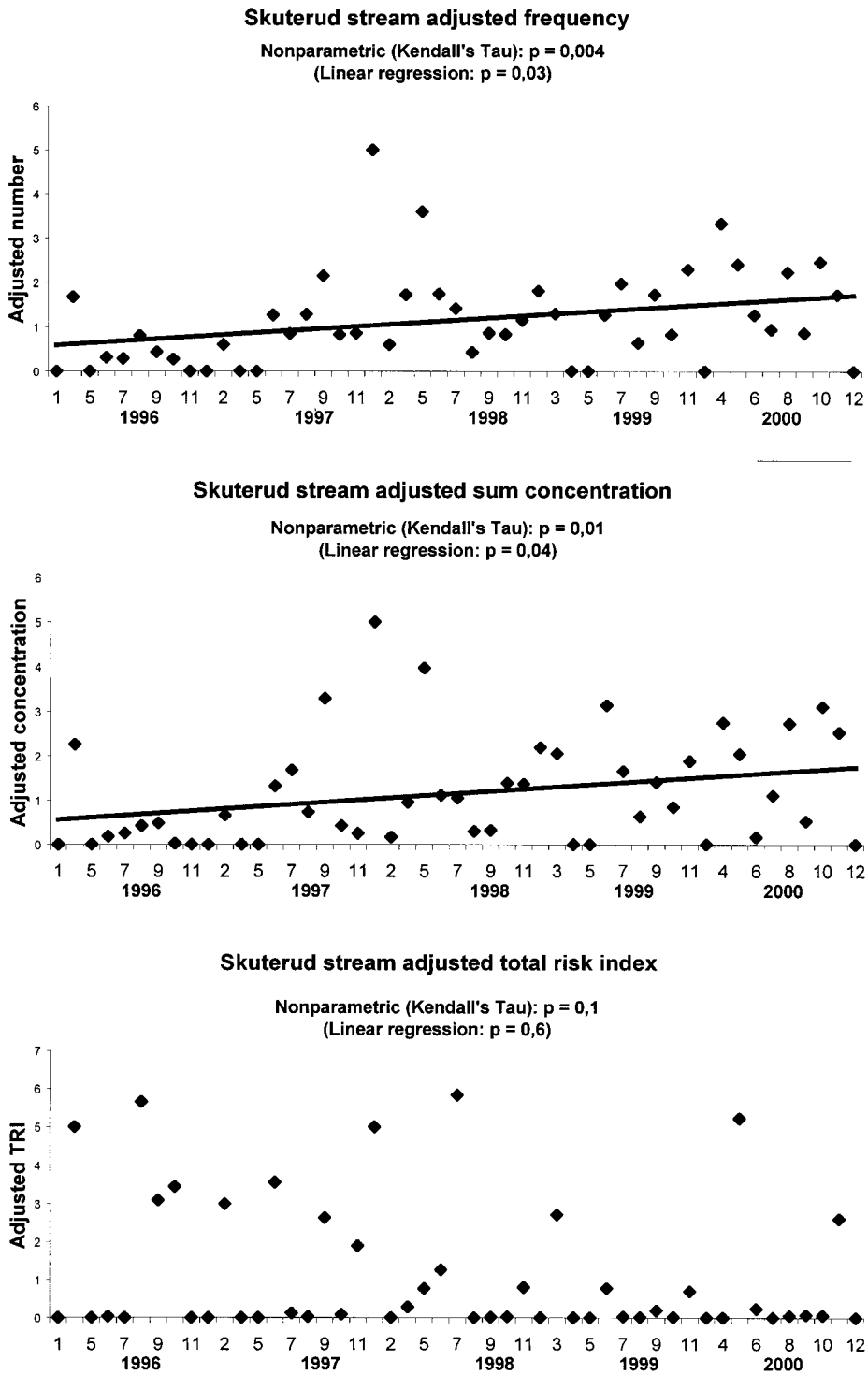

FIGURE 6 Results from trend analyses in Skuterud stream.

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