MAURITIUS RESEARCH COUNCIL
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MONITORING OF PESTICIDE RESIDUE CONCENTRATIONS IN GROUND AND SURFACE WATERS OF MAURITIUS

Final Report

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MONITORING OF PESTICIDE RESIDUE CONCENTRATIONS IN GROUND AND SURFACE WATERS OF MAURITIUS

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SUMMARY

The appearance of residues of nine herbicides. namely atrazine. diuron. hexazinone. 2.4-D. linuron. ioxyntl. paraquat. oxylluorfen and picloram which are often used in weed control in st1garcane and of one insecticide (carbofuran) were monitored al fortnightly intervals during 1995 and 1996 in groundwater from 20 boreholes representing the 10 main groundwater basins of Mauritius and in surface water at 25 locations along the rivers forming part of the Cra nd River North West catchment area. The data showed that only the residues of the follo,ving three herbicides : atrazine. hexazinone and diuron. could be detected in freshwater sources in Mauritius. More than 60% of the groundwater analysed(> 50% for river water) in fact did not contain any herbicide residue. Even when present. the levels of the herbicide residue were mostly within the range of 0.05 to 0.5 ppb. More importantly. their highest c-onceru rauon recorded rarely cxccccdcd the recommended maximum limits of 3 ppb atrazme. 14 ppb diuron and 210 ppb hexazinonc.

The lrcqucncy or appearance of the herbicide residues is not related to the piezomelric depth of the groundwater and to the lime of herbicide application. High intensity rainfall events had a greater impact than period of application on the appearance of herbicide residue il1 the ground and surtacc waters. Nevertheless though U1e period of herbicide application alone had little bearing on the pollution or freshwater sources by herbicides in Mauritius. the level of the rcsrducs in rivers fed by runoff water frorn adjoining fields rose as the urne interval between dat c or herbicide application and the arrival of the high intensity rainfall shortened. The present study therefore showed that although no freshwater source in Mauritius is sheltered fruru possible cont amtnatton by herbicides used in sugarcane. the public fear and mistrust of herbicides used in Mauritius are not justified as U1e level of herbicide residue in water would not pose a risk to human health.

INTRODUCTION

All pesticide compounds are lo a greater or lesser degree chemically tailored to be toxic. On account of that toxicity the presence of detectable concentration of the pesticide residues in surface and groundwaters has caused concern in Europe and the USA about possible effects on human health. Indeed ingestion of pesticide residues has been associated with health problems such as cancer. birth defects and sterility (Bouwer. J990). Herbicides arc the class of pesticides most trcqucntly detected in water sources (Fawcett *et al.* 1994). In Mauritius. from a s,,rvcy of herbicide use by the sugar cane planting community. the amount of herbicide applied annually lo sugarcane in lerms of cornmerctal product per hectare averaged 15 kg. This intensive use of herbicide in sugar cane cultivation has also aroused so much public concern in Mauritius that Government was induced to enact in 1991 an Envtrorirnent Protection Act recommending water quality slandards and permissible limits of pollutanls in surface and groundwaters.

Though studies by Umrit *et al* (J992) and by Umrtt and Ng Kee Kwong (1995) have shown that the herbicides were so rapidly degraded in soils tha.l lheir resulting levels in fresh water sources in Mauritius cannot be high enough lo pose a risk to human health. a.clual herbicide residue levels in ground and surface waters do nol exisl lo support that claim. The determtnauon of lhe real extent of herbicide contarmnauon of freshwater sources in Maurilius is thcrctore of vital interest lo dissipate public concern on herbicide use in sugarcane cultivation. Moreover. the present intensive use of herbicides i11 Mauritius will. in lhe long run. become unsustainable if pollution problems associated with current agricultural practices do exist and arc to remain unknown and unsolved.

The present study was therefore initiated by MSIRJ and Central Waler Aulhorily lo obtain a clear ptcture concerning U1e presence of herbicide residues in natural waters of Mauritius. Specific objectives were :

i. to collect good quality data on the concentration of herbicide residues in the hydrological environments of Mauritius. and

ii. to relale empirically the measurable concentrations of pollutants with the agricultural act ivitics within one hydrological domain.

MATERIALS AND METHODS

Waler from the 20 boreholes listed in Table I and representing the 10 main groundwater basins were sampled al fortnightly intervals. In addilion to the boreholes. water was also sampled every tortrught at 25 locations on the 8 rivers in the Grand River North West (GRNW) catchment area. the second largest drainage area (113.4 km2) having as main river the GRNW. The local ion of sampling points on the rivers is also listed in Table 1. Reasons for focussing on the river waters of the GRNW catchment area were two-fold : firstly. the rivers (except River Ser he and River Mcsnil) of that catchment area are feel mostly by run-off from adjoining fields (Central Waler Authority. 1993) and peslicicle run-off from agricultural fields is known to be an in,porlanl cause of environmental pollution (Wauchope. 1996). Secondly. as the sugarcane lands bordering rivers such as River Cascade are all cultivated by the sugar estates. records of rates. types. and period of application of the herbicide as well as daily rainfall are easily accessible tor relating appearance of herbicide residues in the river waler with chemical weed control practices in sugarcane.

Immediately after collection. the water samples were treated with I mL of 10 mg/L mercuric chloride solulion and stored at 4°C until extraction and analyses of the residues of the herbicides (listed in Table 2). which are frequently used in sugar cane fields.

The analytical techniques for the measurement of herbicide residues were adapted from methods already existing in the literature. Thus herbicide residues were determined by solid phase extraction (SPE) followed by high performance liquid chromatography (J-IPLC) using diode array deleclion (DAD). The limits of detection and recovery of the 9 herbicides and of carboluran inscclicide were as lollows :

Herbicide	Detection limit (ng/L)	% recovery (at 20 ppb)
Atrazinc	50	90.1±1.8
Hcxaztnone	50	86.8 ± 11. I
Dturori	50	90.6 ± 2.8
Li1111 run	50	77.4 ± 5.5
2.4-D	50	95.2 ± 3.5
loxynil	50	99.5 ± 2.8
Paraquat	250	88.6 ± 5.5
Oxylluorfen	50	82.0 ± 5.0
Picloram	50	88.5 ± 3.9
Carboturan	100	84.9 ± 5.8

RESULTS AND DISCUSSION

Herbicide residues *found in water*

Over the two year monitoring period (1995 and 1996) a total of 746 groundwater and 1025 river water samples were analysed for residues of carbofuran and of the 9 herbicides in Table 2. The rcaults obtained showed that residues of only the three herbicides - atrazfne, **hexazinone** and diuron - could be detected in the ground and surface waters. These three herbicides are ,1111ong those most used in sugarcane lands (Figure !). However. the presence or a herbicide in the ground or surface waters was not related to the rate or total quantity used. In this context though 2.4-D is one of the herbicides used in largest amount in Mauritius with as much as 2 k.K a.i applied per hectare. it has not been detected in the waters during 1995 and 1996. Yet 2.4-D has commonly been reported lo be present in ground water elsewhere. e.g in the United Slates (Vcch *el. al.* 1996).

Tile absence of 2.4-D in ground and river waters concurred with results of degradation studies reported by U111ril and Ng Kee Kwong (1995). They showed that, 2.4-D was rapidly degraded in soils with 65-80% of the applied amount disappearing in less than I week. Hexaztnone, on the other hand. was found to be very persistent with 13-16% of the quantity applied (0.75 kg a.i/haJ still present 48 weeks after application. The presence or hcxazinone residues in freshwater sources in Mauritius should consequenUy not be surprising despite the fact that the average rate or hcxazinone (0.6 kg a.i/ha) commonly used is lower than that or 2.4-D. The frequent appearance of a trazrne residues in ground and river waters of Mauritius is in agrccn1cnt wtt h observations from the numerous water morutortng programs in Europe and the USA where atrazine on account of its persistence in soils is one 0f the most commonly detected herbicide (e.g Richards *el al.* 1995: Bmtern and Devillers. 1996).

Frequency of appearance and level of herbicide residues *in water*

It must be emphasized that the residues or the 3 herbicides (atrazine. hexazinone and diuron) were not present in evely ground or river water analysed during 1995 and 1996. In fact more than 60'V., or the ground water samples (50% for river waters) did not contain any herbicide residue (Figure 2). Even when the herbicide residues were present. their concent.ralions were most often in the lower limits (0.05-0.5 ppb) measurable by the HPLC (Figure 3). More irnportanl ly the data provided evidence that U1c highest level of any or the herbicide residues in ground waler (Figure 4) would not exceed the recommended maximum limit or 3 ppb atrazine. 14 ppb diuron and 210 ppb hexazinonc. This was lo be expected since lysuneter leaching studies had already shown that even in waler draining at 1 m soil depth the concentration of herbicide residues was already low and never exceeded or maximum perrnisstble lirnlts

rccornrncndcd in the 1991 Environment Protection Act (Umril *et al.* I 992: Umrit and Ng Kee Kwong. 1995). As downward movement of the herbicide residue lowarcls the aquifer continues.
thcir concentration is expected to be further depressed by processes of dcgradalion and sorption by soil components. The highest observed conceritrauons of herbicide residues in rivers feel mainly by run-off water from acijoining llelds could however rtse above the maximum rcconuncndcd limils as shown in l"ig 5. Indeed during the sludy period of 1995 and 1996 the recommended limits or 3 ppb atrazine and 14 ppb diuron had been exceeded on two and three **occasions. respectively.**

Though the present study focussed on the detection of the parent herbicide compound. it was however aware from studies elsewhere (see e.g Baluch *et al.* 1993: Mouvel and Moreau. 1997) that degradauon products of lhe herbicides could be more important contaminants in the soil **and** water **environments. Degradation of atrazinc. for instance. produces** metabolites **such as** dccthylauazrne and deisopropylatrazrne which are just as loxic as the parenl compound (Fcrmamch *el al.* 1996). Water moniloring studies as reviewed by Baluch *et al* (1993) have **further** demonstrated **that the atrazine degradation products can occur alone or in** combination with the parent atraztne . Though metabolites of at..razine could occasionally be detected (based a specl ral analysis) in the prescnl study their concenlrations were however invariably always much lower t**han** that **of the parent** atraztne **compound. 1..he risk of** contamtnation **of river and** grou1JCl waters by metabolttes of atrazme could therefore be safely ignored.

The fact thal herbicide residues of either alrazine or hexazinone or diuron have been detected **at the** some mornent **in** urne **in water** from **every borehole** monitored **and at each of the 25 locations on lhe rivers of U1e Grand** River **North West** catchment **area indicates that no fresh** water **source in Mauritius is sheltered** from **pollution by herbicides used in sugarcane weed control.** The **rrcqucncy of** coruarrunatton **of the water sources. however differed. Saine** boreholes such as BH 392 at Highlands contained herbicide residues more often than other boreholes such as BH 59 al Solferino (Figure 6). This observation is equally true for river waters, c.g River **Profonde was more frcquenlly polluted by herbicides residues than River** Mcsrul (**Figure** 7**).**

Effects of piezometric level, application time and rainfall on residue *appearance* in *water*

The frequency of groundwater contamination by herbicide residues was not, relaled lo the ptezomerrtc depth of the groundwater basin. Indeed il should nol be believed that the deeper the waler table the less conlaminated or the less often would U1e water contain herbicide residues. As illustrated in Figure 8 water drawn al more than 30 m depth from borehole BH 12 at Plaines des Papayes contained herbicide residues on more occasions during 1995 and 1996 lhan Ihe water found less than 8 m deep in borehole BH306 at Morcellement St Andre. The appearance or herbicide residues in deep water tables should not be surprising. Microbial populations which control the fate and transport of the contaminants decrease with soil depth thus enhancing U1e likelihood of persistence of mobile compounds that have moved out of the biologically active surface layer (Veeh *et al.* 1996).

The data in Figure 8. in addition. serve to highlight the fact that no consistent time period existed for lhe appearance of herbicide residues in natural waters in Mauritius. Thus while no diuron residue was dctected in February/March 1995 at Plaines des Papayes. U1e residue was present in water from that same borehole at corresponding time in 1996. The lack of any flxed period during the year for herbicide residues to be detected in the ground and river waters showed that lhe time of application of herbicides in sugarcane fields on its own had little bearing on U1e appearance of herbicide residues in the water sources of Mauritius. Irrespective of Ihe climatic or geographical zone herbicides are most intensively used during the period August lill November (Figure 9) and yet herbicide residues were often not found (Figure IO) in groundwater during that active period of chemical weed control in sugarcane. In contrast. studies done elsewhere with crops other lhan sugarcane have shown the level of herbicide residues in waler lo depend upon the season with maximum concentration found during U1e period when the crops were planted [see e.g Bintein and Devillcrs. 1996. Kimbrough and Litke.
1996).

The **appearance of herbicide residues in ground and river waters in Mauritius is foremost a** function or high rainfall events (Figure 10). This dependence on rainfall had in fact also been observed elsewhere [e.g Bowman *et al.* 1994: Shiptalo *et al.* 1997). High intensity rain. in particular when it occurred shortly after herbicide application. would quickly move the herbicide residues beyond the rooting zone before they could be degraded by microorganisms. Low intensity rain would primarily move the contaminants into the soil matrix where they would be less subject to leaching and are bypassed by water flowing in macropores (Sigua *et al.* 1995). The appearance or herbicide residues in the groundwater would however nol occur during or immcdialely after the high rainfall events. Sorption/desorption interaction or herbicide molecule with the soil components retard the movement of the herbicide relative to that of water as was found in U1e lysimeter studies by Umrit and Ng Kee Kwong [1995). On account of the retarded movement of the herbicides in the soil. their residues appeared in the groundwater days after the high rainfall event (Figure 10).

The lag period discussed above between rainfaU event and herbicide residue appearance did nol exist for rivers feel by water runoff from adjoining fields [Figure 11). Thus examination of the levels of diuron in River Cascade. for example at Camp Auguste. showed the presence of high diuron concentration in December 1995 because high rainfall events lhal month happened shortly after lhal herbicide was applied to lhe neighbouring fields. Studies by Bowman *el al* (1994) and Gaynor *el al* (1995) had already demonstrated that the herbicide losses in run-off tend lo be greatest for the first rainfall arriving soon after application. On the other hand liltJe alrazine was detected in River Cascade in December 1995 because the period of its application in September 1995 were relatively dry with no rainfall of sufficient intensity to produce runoff (rigure 12).

CONCLUSION

The present study indicates that all fresh water sources in Mauritius may be contaminated by residues of utraztne. diuron and hexazinone after a high rainfall evenl. As lhe highest level of these herbicides residues in the ground and river waters was generally well below the recommended maximum limits for ground and surface waters. these three herbicides do not pose a risk lo human health. There is therefore no justification for lhe existing public fear and mtsrrust of herbicides used in sugar cane cultivation in Mauritius.

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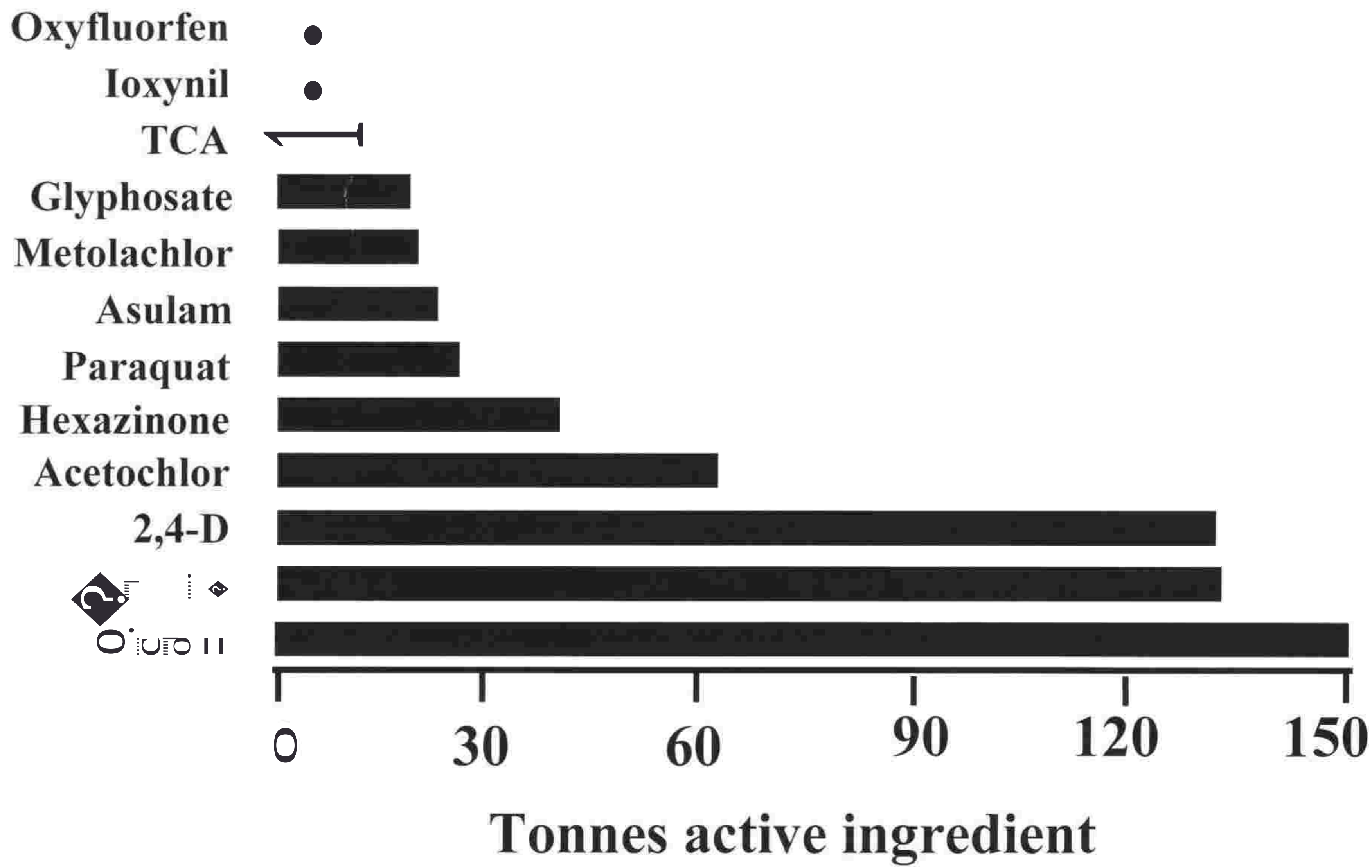


Fig 1. Herbicide use in Mauritius

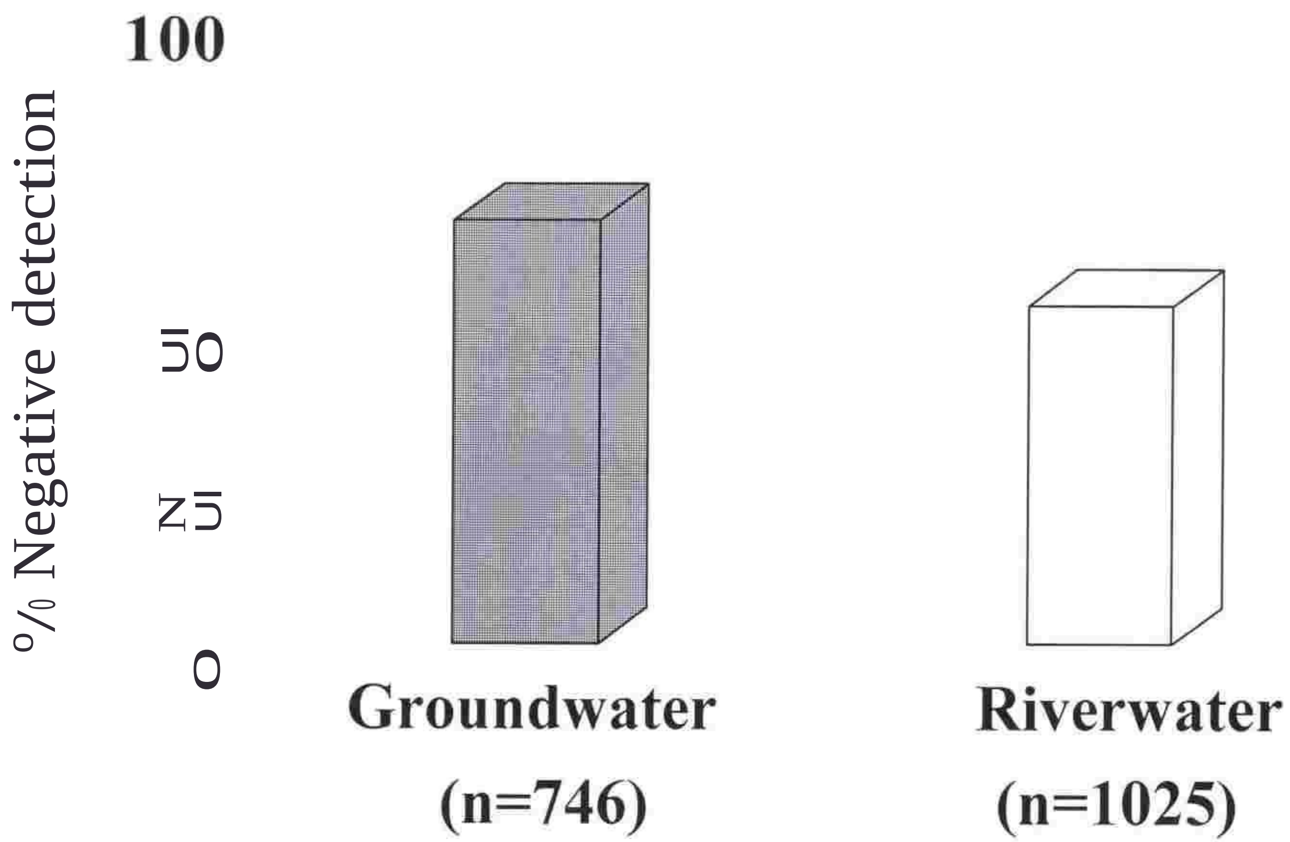
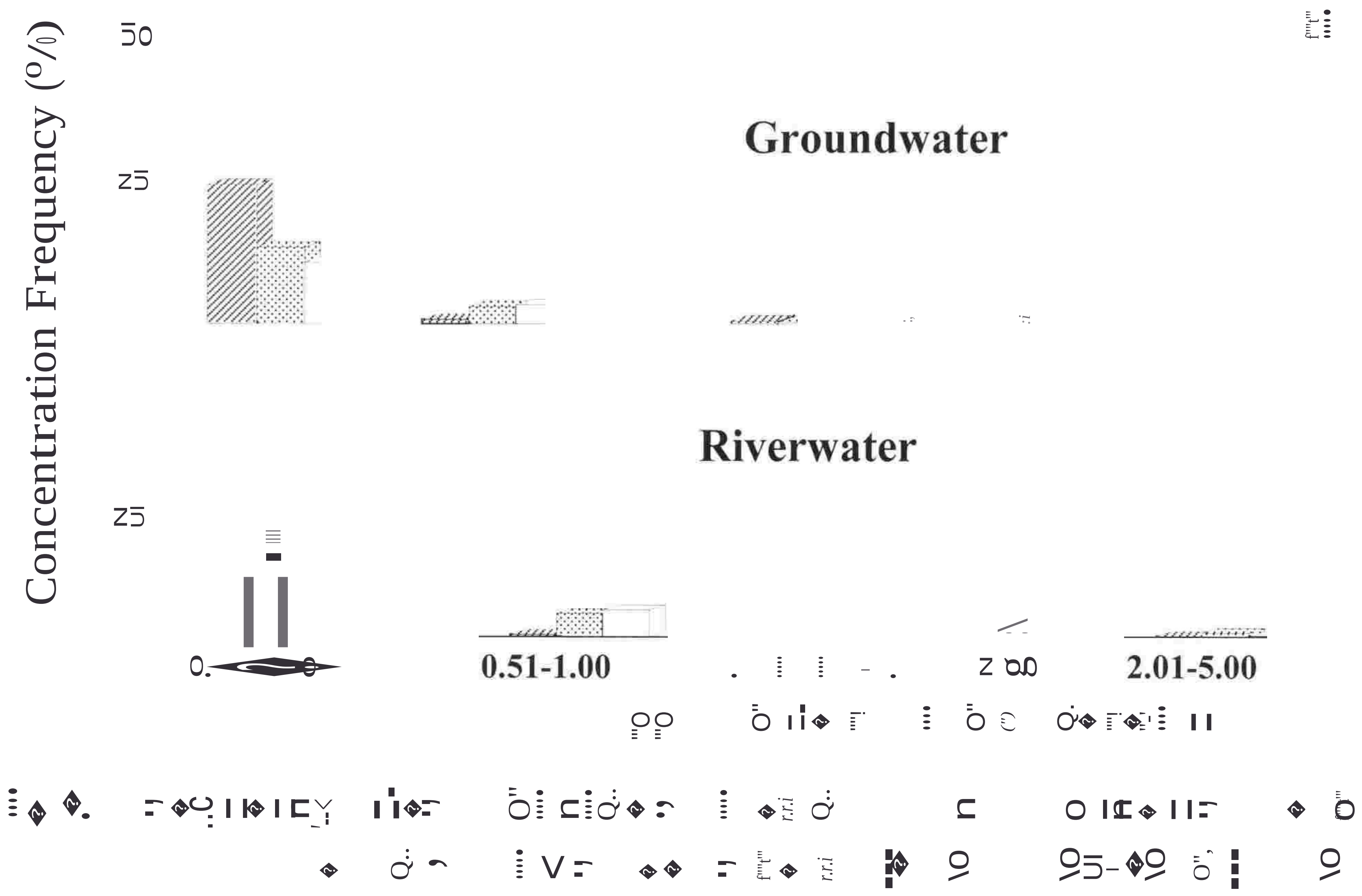


Fig 2. Negative detections in ground and river waters (1995-1996)


Concentration Frequency
Groundwater
Riverwater
0.51-1.00
2.01-5.00

ATRAZINE
DIURON
HEXAZINONE

Fig 4. Highest herbicide residues levels in groundwaters (1995-1996)

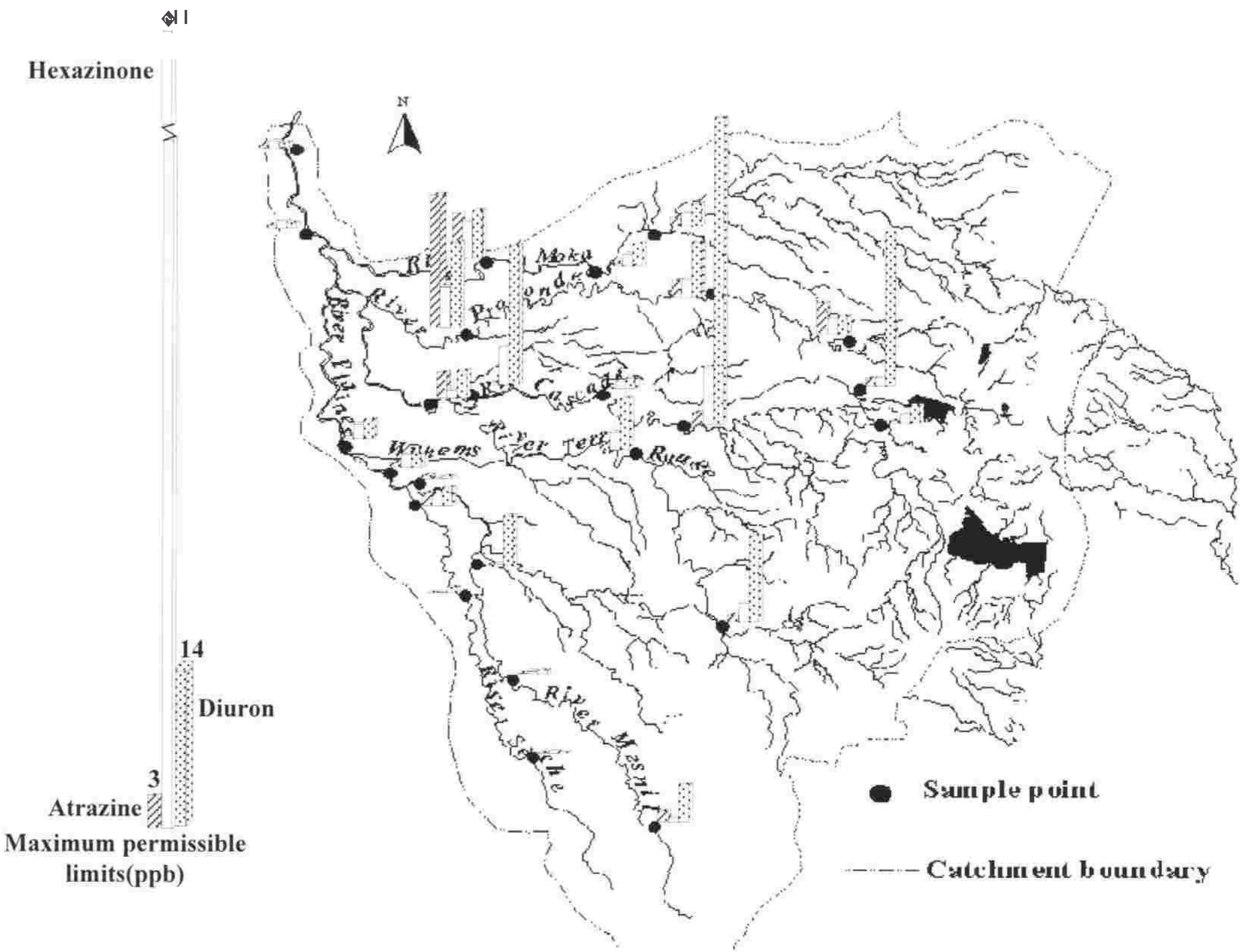


Fig 5. Highest herbicide residue level in riverwaters of GRNW catchment area during 1995 and 1996.

ppb herbicide residue

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ppb herbicide residue

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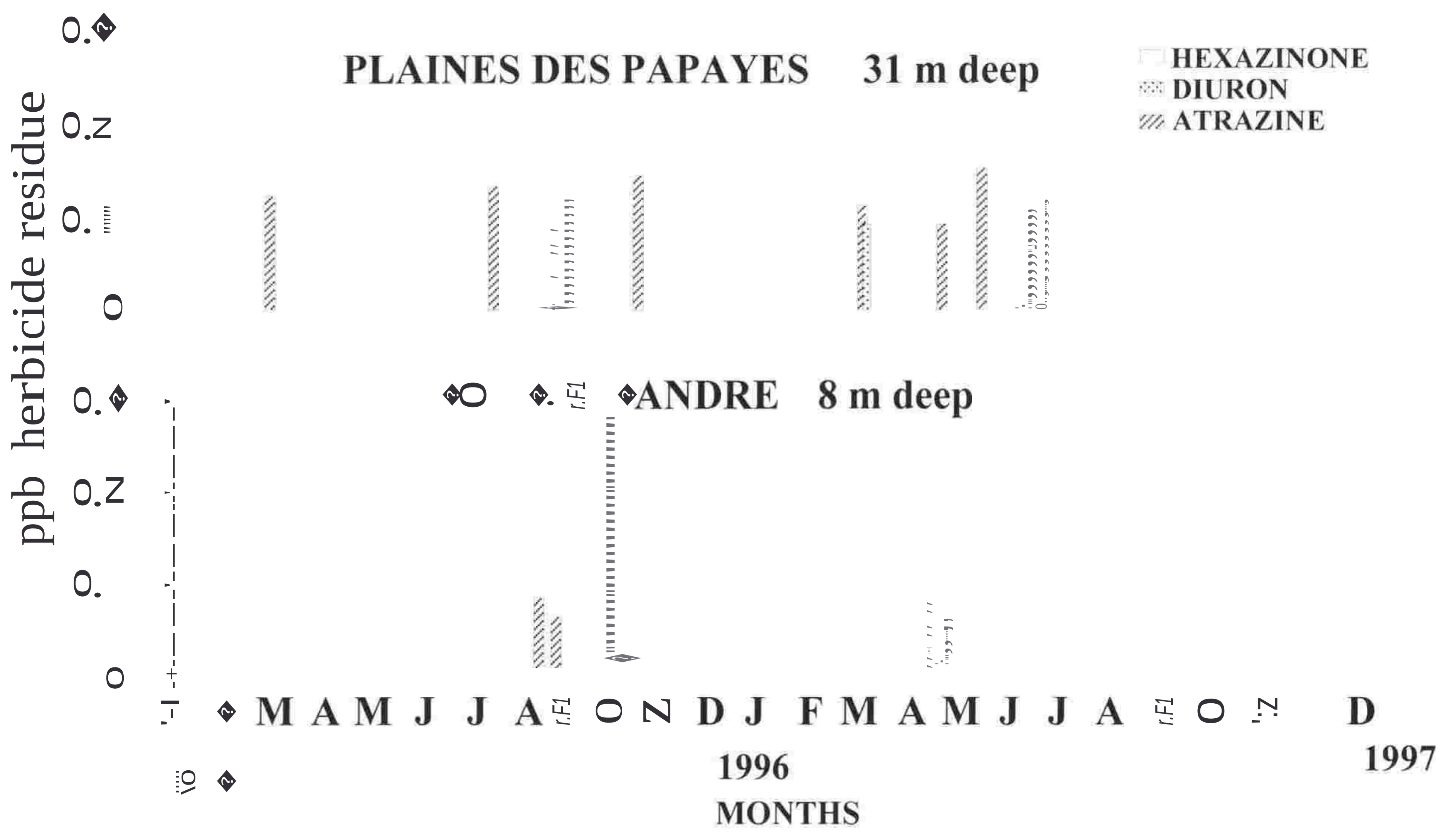
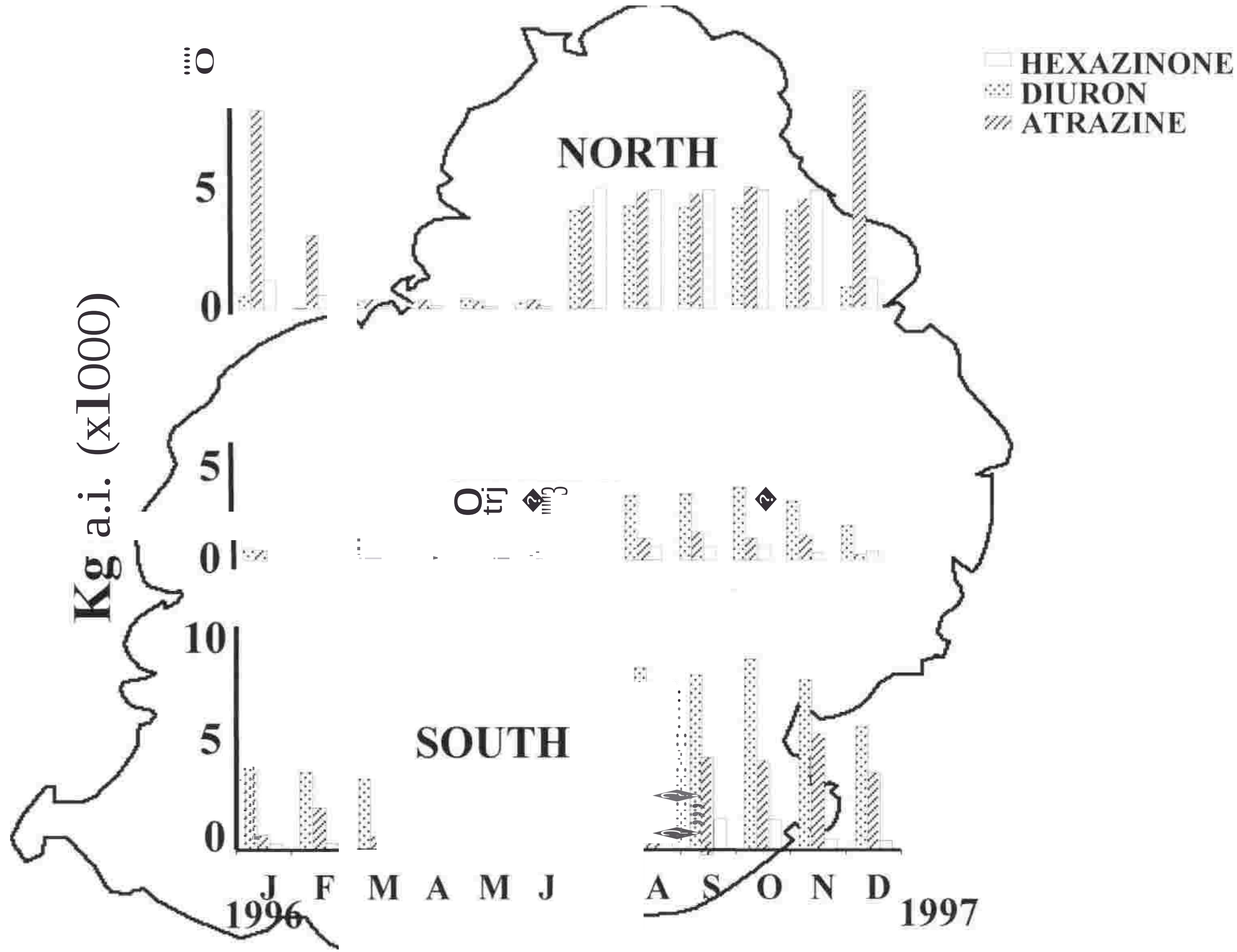


Fig 8. Herbicide residue appearance in groundwater sampled at piezometric depth (31m and 8 m) during 1995 and 1996.


Kg a.i. (x1000)
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1997

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ppb diuron
Kg a.i
Rain (mm)

[illegible]

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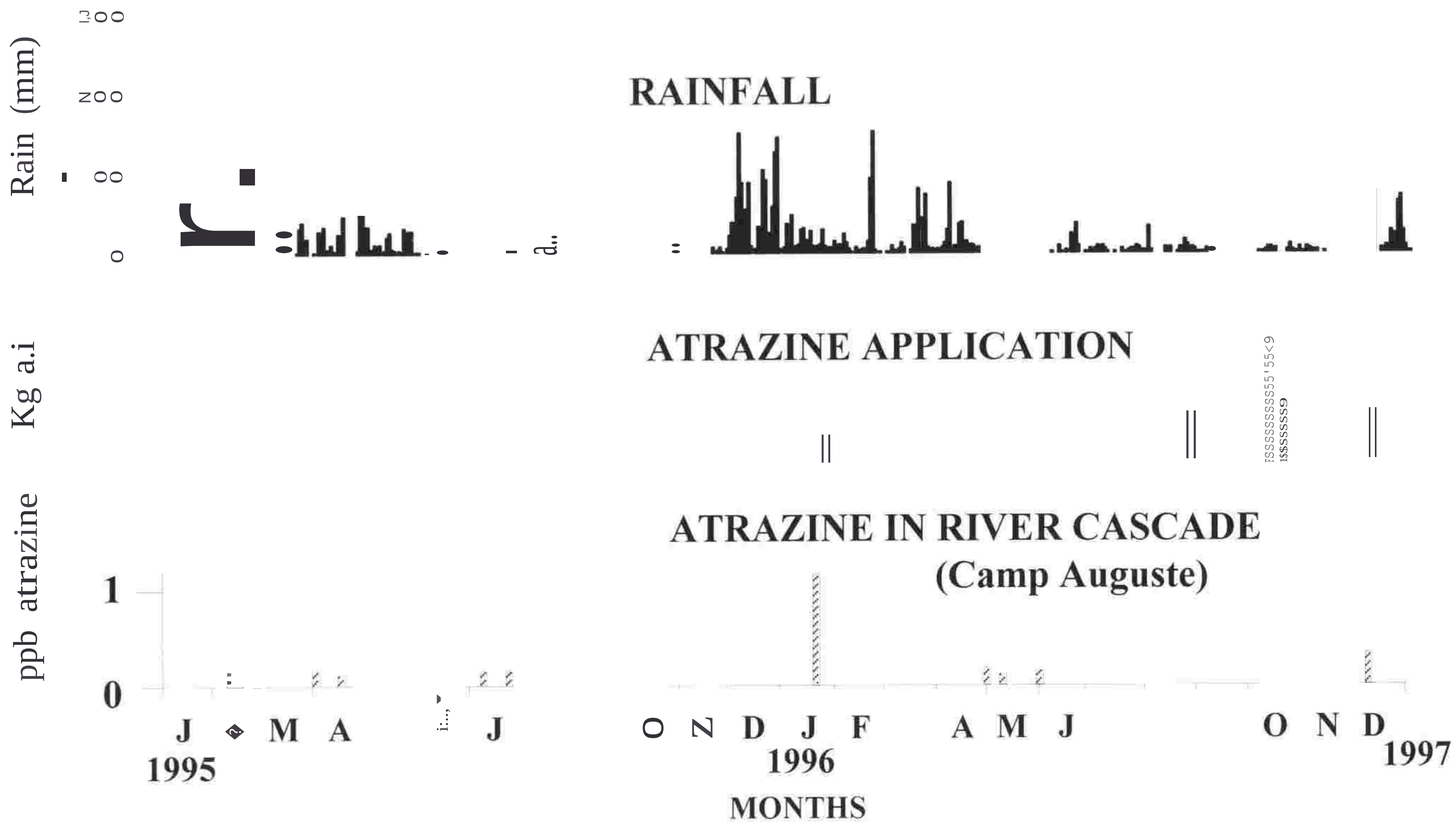

Fig 12. Atrazine appearance in riverwater at Camp Auguste in relation to rainfall and application time