

CHAPTER 10

GENERAL DISCUSSION AND CONCLUSIONS

More than three decades of research on atrazine have accumulated a wealth of data and yet occasional loss of selectivity (Le Court de Billot & Nel, 1985) and excessive persistence (Riley, 1991; Del Re et al., 1991) are encountered. Decreased selectivity is associated with increased bioactivity, usually as a result of excess amounts of the herbicide at the site of action in plants. This type of damage to crops is virtually unpredictable, except where overdosing is known to have occurred. In contrast, potential damage due to carry-over of residues can be predicted by considering factors which influenced herbicide dissipation from soil during the period after its application until the next crop is planted. It is important for crop producers to know if there are any limitations or restrictions in the sequence of crops that can be grown after using atrazine. Therefore considerable information is required regarding crop sensitivity (e.g. residue concentration thresholds for different crops), herbicide stability, mobility, adsorption/desorption relationships and transfer between the different environmental compartments.

Research on factors implicated in apparent atrazine damage to maize during the 1981/82 and 1982/83 growing seasons was concluded with work on aspects of nutrient supply. Maize seedlings which showed symptoms of N, P, K, Ca and Mg deficiencies (Chapter 2) were actually affected less by atrazine than seedlings supplied with adequate amounts of nutrients, probably due to greater uptake of the herbicide by control plants in which



life processes proceeded normally. The finding of Sosnovaya & Merezhinskii (1979) that maize plants growing in a nutrient-deficient medium showed less tolerance to atrazine than plants supplied with optimal levels of nutrients was not substantiated. The observed tendency (statistically insignificant) of increased sensitivity to atrazine which was displayed by seedlings deficient in Mg could possibly be ascribed to the vital function of this element in the chlorophyll molecule. Atrazine inhibits electron transport during the light phase of photosynthesis (Fuerst & Norman, 1991), and therefore both insufficient Mg and high amounts of atrazine could conceivably have acted together in reducing maize seedling tolerance to atrazine. From the viewpoint of carry-over of atrazine this aspect warrants further investigation, since crops that are inherently susceptible to atrazine may show greater responses to the particular combination of atrazine and Mg than would maize.

The purported inhibiting effect of high P supply on photosynthetic CO₂-fixation (Claassens & Fölscher, 1985) was not substantiated in work reported in Chapter 2. High P levels in maize seedlings did not sensitize them to high levels of atrazine, as would be expected if a synergistic effect was involved. This is in contrast with the finding of Stolp & Penner (1973) that synergism between atrazine and high phosphorus caused increases in respiration and reductions in net photosynthesis of maize plants. It is improbable that nutrient imbalances of the order of those investigated in Chapter 2 could have played a role in the damage caused to maize in the field. The localized and isolated nature of that incident probably excludes both macro- and micronutrients as causative factors, and more likely points to a combination of soil and weather factors which caused phytotoxic amounts of atrazine to accumulate in maize seedlings.



Experiments conducted to evaluate the susceptibility of dry beans (cv Teebus), grain sorghum (NK 222), oats (SWK 001), soybeans (cv Forrest) and sunflower (cv SO 222) to atrazine showed that the species differed in their susceptibility to the herbicide. Also, results demonstrated that the herbicide threshold concentration for a particular species varied from soil to soil (Chapter 3). Thus the need to associate measured amounts of atrazine, or its phytotoxic residues, with responses of sensitive crops was highlighted. For carry-over risk assessment purposes the need for more information on the relative availability of atrazine residues in soils, as well as on species differences in susceptibility, have been stressed by Stalder & Pestemer (1980), Pestemer, Stalder & Eckert (1980) and Pestemer *et al.* (1983). Blanket atrazine threshold values for crops would have little or no value in deciding which crop to plant in soil containing the herbicide and/or its phytotoxic residues, since different amounts will be available to a particular crop in different soils. Threshold values determined under similar conditions (e.g. by using a single soil) should provide reliable orders of susceptibility for different species, or even cultivars.

Comprehensive research has been conducted locally on factors which influence the bioactivity of atrazine (Smit *et al.*, 1977, 1979, 1980; Nel & Reinhardt, 1984; Ehlers *et al.*, 1987, 1988), but its persistence in South African soils had not been extensively studied before the present investigation. The short-term (< 30 days) bioactivity study (Chapter 4) confirmed the results of previous work which indicated that organic matter content, clay content and P-reversion (in this order) were more important than soil pH in determining atrazine bioactivity. The subsequent persistence investigation (Chapter 5), which was conducted 182 days after atrazine application, showed that the order of



importance for variables changed with time: organic matter content > soil pH > P-reversion > clay content. Only the role of organic matter content remained constant. Probably the most significant result was the apparent importance of soil pH as a predictor of persistence, in contrast to its poor prediction of short-term bioactivity. The finding on the importance of soil pH on the persistence of atrazine corroborated results reported by Armstrong *et al.* (1967), Roeth *et al.* (1969), Best & Weber (1974), Hiltbold & Buchanan (1977), Smit *et al.* (1979, 1980) and Walker *et al.* (1983). Generally, it was reported that atrazine stability increased with increasing pH-levels. Adsorption on colloids such as organic matter apparently provides protection against degradation. Increasing half-lives with increased adsorption have been reported for atrazine (Burkhard & Guth, 1980). Moyer, Hance & McKone (1972) found lower degradation rates for atrazine in soil amended with activated charcoal.

The fixed recropping intervals that apply when atrazine is used in maize restrict recropping options, or crop choice in cases of forced recropping. Results reported in Chapter 6 showed that recropping intervals could be refined by considering soil properties which determine atrazine persistence. It was also shown that the present classification of crops for recropping purposes, according to their perceived sensitivity to atrazine, requires re-examination. Even cultivars within species may differ in tolerance to atrazine. Stalder & Pestemer (1980), Pestemer *et al.* (1980), Gottesbüren *et al.* (1991) showed that information on the relative susceptibility of rotational crops to herbicide residues, as well as the availability of residues for uptake by crops, would improve forecasts of recropping risks.



Chemical analysis by means of HPLC (Chapter 7) showed that the persistence of atrazine varied between two diverse soils, despite the exclusion of leaching as a factor. It was suggested that the relatively high pH and the high adsorptive capacity of the montmorillonite clay soil restricted the breakdown of atrazine in that soil. High atrazine stability at neutral pH (Hiltbold & Buchanan, 1977; Appleby, 1985) and apparent protection against degradation through adsorption on colloids (Burkhard & Guth, 1980) have been reported. The well reported roles of soil water content and temperature (Walker & Zimdahl, 1981; Walker & Allen, 1984; Walker, 1989) in the persistence of this herbicide were substantiated. Of the two weather factors, soil water content had the dominant effect, despite leaching being negated. The faster breakdown rate that was observed at the field capacity soil water level, compared to the rate in airdry soil, suggests that processes which require water, e.g. desorption, hydrolysis and microbial degradation, were probably involved.

Chemical analysis makes detection of herbicide residues possible in all compartments of the environment, but the measured amounts still need to be linked to the responses of different crops (Gottesbüren et al., 1991). The bioassay technique that is described in Chapter 8 could be used to estimate phytotoxic atrazine residues in soils, provided the residue concentrations are of such an order that an indicator species responds neither too strongly nor too weakly. In view of the perceived disadvantages of both techniques, a combination of bioassays and chemical analysis would be ideal for prediction of carryover effects on sensitive crops.



Many computer simulation models are available for quantification of herbicide residues in soils, even at different depths, before the following crop is planted (Walker & Barnes, 1981; Gottesbüren et al., 1991). Amongst the many information inputs required for these models to produce reliable estimates, is the half-life of a compound in soil. As half-life values that are used in models are usually gleaned from published data of other workers, predictability may be reduced. The aim of the work reported in Chapter 9 was to improve the situation for atrazine by at least taking into account the variability of its half-life in different soils. Results of the experiment in which the role of soil pH in atrazine persistence was investigated (Section A in Chapter 9) confirmed conjectures in previous experiments about the role of pH. It was found that atrazine persistence increases with increased soil pH. The subsequent experiment with 25 soils (Section B in Chapter 9) confirmed the importance of soil pH on the herbicide's persistence. Soil organic matter content was the most important predictor of the bioactivity (Chapter 4) and persistence (Chapter 5) of atrazine. In Chapter 9, organic matter content was not of prime importance in the prediction of atrazine persistence because leaching was negated in that investigation. An insignificant role for P-reversion was found in Chapter 9, in contrast to the findings in Chapters 4 & 5. The reasons for this are not obvious, and may remain unexplained until more about the mechanism involved in the purported interaction between the Al.Fe.OH-component of soil and atrazine molecules is known. The culminant multiple regression model, which was derived in the incubation study (Section B in Chapter 9) for the prediction of atrazine half-lives in soils will hopefully reduce reliance on categorized half-life values that are given in textbooks and other reference material.



Failure to establish the exact causes of the purported atrazine damage to maize as far back as 1981/82, illustrates the complexities involved in studies on the environmental fate and behaviour of the herbicide. Progress was made in the present study towards identification of factors which influence the bioactivity and persistence of atrazine in soil. Although work on the roles of essential macronutrients in the tolerance of maize to atrazine did not produce positive results, it may be worthwhile to investigate what effects the same treatments would have on the tolerance of normally susceptible crop species. Useful re-confirmation of the importance of certain soil properties on the bioactivity of atrazine was provided in field trials. The persistence of atrazine was studied for the first time in South Africa in both field and glasshouse experiments. With this work the need to refine recropping periods for susceptible crops which follow maize treated with atrazine was highlighted. In other persistence studies the dominating role of soil pH in the determination of atrazine persistence was conclusively established. A regression model which may improve the prediction of atrazine half-lives in soil was presented. It is foreseen that atrazine will remain an important component of weed management strategies in South Africa, and that the need for accurate prediction of its persistence in soil will prevail.



SUMMARY

BIOLOGICAL ACTIVITY AND PERSISTENCE OF ATRAZINE

- 1. Certain aspects of the phytotoxicity and availability of atrazine and its residues for uptake by plants were researched in this study. Bioassays with plants as indicators of the availability and phytotoxicity of atrazine were conducted in glasshouses and in the field. Chemical analysis for measurement of atrazine in aqueous medium and soil were done in three experiments. Emphasis was on the identification of environmental factors, particularly soil properties, which govern the bioactivity and persistence of atrazine and its phytotoxic residues.
- 2. The roles of certain essential macronutrients in the resistance of maize to atrazine was evaluated. Growth-retarding levels of N, P, K, Ca and Mg, individually or in certain combinations, had no significant effects on the crop species' resistance to atrazine. In a separate investigation it was found that the tolerance of maize seedlings to atrazine was neither influenced by high phosphorous (P) application in the root zone nor by relatively high P concentrations in shoots. Results indicate that high amounts of P containing fertilizers in the root zone of maize seedlings are unlikely to sensitize the plants to atrazine.
- 3. It was shown in pot experiments that atrazine threshold concentrations in soil for dry beans, grain sorghum, oats, soybeans and sunflower varied from species to species and from soil to soil. The differential sensitivity of these crops to atrazine infers that



recropping intervals recommended after atrazine use should be based more closely on differences in crop susceptibility. Further research is needed to relate known amounts of phytotoxic atrazine residues in soils to the response of different species, with a view to better assess the risk involved in growing a particular crop where atrazine carry-over occurred.

- 4. The strength of relationships between selected soil properties and the bioactivity of atrazine were investigated in a total of 30 field trials conducted over a one year period at ten trial sites. The initial bioactivity of atrazine which was assessed 35 days after application was best correlated with the organic matter content and P-reversion characteristics of the soils. Clay content and CEC were also important, but at lower levels of significance. These findings confirmed those of several previous investigations which were aimed at identifying predictors of the short-term activity of atrazine.
- 5. Six months after herbicide application in the trials mentioned above (point 4), organic matter content, soil pH and P-reversion predicted 35%, 19% and 14% of the variation in bioactivity, respectively. Both CEC and clay content were poor criteria at that stage. Organic matter content dominated as the best predictor of both the short-term (bioassay on day 0) and longer term (assayed on day 182) bioactivity of atrazine. Indications were that soil pH could also be an important predictor of atrazine persistence. Differences in persistence between trials in close proximity suggest that persistence of atrazine was more closely linked to soil characteristics than to climatic conditions. Results suggest that current waiting periods, which are recommended for specific crops grown after maize in which atrazine was used, can be refined by



distinguishing between soils.

- 6. Atrazine persistence was monitored at 12 and 24 months after application in maize at eight localities in order to evaluate the applicability of the single recropping period that is specified for dry beans and sunflower. The test crops were the dry bean and sunflower cultivars mentioned under point 3. Carry-over of phytotoxic atrazine residues, as judged from the extent of crop yield reduction, varied considerably from site to site. In a wide range of soils the sunflower cultivar was generally less tolerant to atrazine than the dry bean cultivar, thus confirming the relative susceptibility of these crops to atrazine (see point 3). With the exception of a montmorillonite soil in which significant carry-over occurred, no significant damage to the dry bean cultivar was incurred on soils in which kaolinite clay predominated. Results suggest that the current recropping intervals for crops which are sensitive to atrazine could be refined by assigning different recropping periods based on soil and species differences.
- 7. The influence of temperature and soil water content on the persistence of atrazine in a clay soil and a loamy sand soil was investigated under controlled conditions. Atrazine was measured by means of high pressure liquid chromatography. The half-life of atrazine in the loamy sand was reached after about 60 days, whilst at the same stage 70-75% of the applied atrazine remained in the montmorillonite clay soil. Virtually no degradation of atrazine occurred in air-dry soil. Degradation in both soils at field capacity soil water was significantly higher than in air-dry soil. Increases in soil water from field capacity to 2x field capacity had little or no effect on persistence. The lowest temperature regime slowed the rate of degradation of the herbicide in the light



soil only. In this experiment soil type and soil water content had greater effects on the degradation rate of atrazine than temperature.

- 8. A simple bioassay technique was used to study the residual activity of atrazine applied at 0.25 kg ai ha⁻¹ in samples taken from different depths in a sandy clay loam soil. It was estimated by means of dose-response curves that 55% of the amount applied in the field was present in the 200-300 mm soil layer on day 30 after application. At days 60, 90 and 120 the percentages remaining in the 200-300 mm soil layer were about 3%, 2% and 3%, respectively. Estimates on day 120 indicated that 2% of the amount applied remained in the top (0-100 mm) soil layer, and 6% in the 300-400 mm layer. There was generally good correlation between visual and measured assessments of damage in the field. The bioassay technique could be convenient for estimating atrazine residues in the soil profile, especially to predict the potential for damage to sensitive follow-up crops.
- 9 (a). The relationship between soil pH and atrazine persistence already reported above was demonstrated again in an experiment where soil samples treated with atrazine were incubated for different intervals over a period of 120 days. Essentially only the pH(H₂O) levels of these samples were different. Atrazine persistence was shown to increase with increasing soil pH, thereby substantiating findings of increased stability of atrazine in high pH soils.
- 9 (b). Dose-response curves were obtained with the test plant oats (cv SWK 001) for 25 soils, and used to estimate amounts of atrazine, or its phytotoxic residues, in these



soils 0, 30, 60, 90, 120 and 150 days after application of 0.2 mg atrazine kg⁻¹. The rate of atrazine degradation in each soil was subsequently plotted (mg atrazine kg⁻¹ against number of days after treatment). From the quadratic formulas of these relationships, atrazine half-lives were estimated, i.e. the number of days required for the applied amount to be halved. Regression analysis showed that the square of soil pH was the best predictor of atrazine persistence. Soil pH and organic matter content (% C) were the only variables which qualified for inclusion in a multiple regression equation for prediction of atrazine persistence. It is proposed that half-lives of atrazine in soils can be predicted with the following regression equation:

$$y = -2.29 + 1.77x_1 + 20.81x_2$$

where $y = \text{half-life in days}$; $x_1 = [\text{soil pH(H}_2O)]^2$; $x_2 = \%$ C

Results generated in this study should contribute to knowledge of the factors which govern the bioactivity and persistence of atrazine in soil, and therefore, hopefully improve the predictability of both phenomena.



OPSOMMING

BIOLOGIESE AKTIWITEIT EN NAWERKING VAN ATRASIEN

- 1. Sekere aspekte van die fitotoksisiteit en beskikbaarheid van atrasien en residue daarvan vir opname deur plante is ondersoek. Biotoetse met plante as indikatore van die bio-aktiwiteit van atrasien is in glashuise en op die land uitgevoer. Chemiese analise van grond- en watermonsters vir atrasien is in drie proewe gedoen. Die klem van die studie was op identifisering van omgewingsfaktore, en dan veral grondeienskappe, wat bepalend is by die bio-aktiwiteit en nawerking van atrasien en die fitotoksiese residue daarvan.
- 2. Die verdraagsaamheid van mieliesaailinge teenoor atrasien is in vloeistofmedium ondersoek. Tekorte aan N, P, K, Ca en Mg, afsonderlik of in sekere kombinasies, het by hoë atrasienkonsentrasies nie betekenisvolle verskille in die verdraagsaamheid van saailinge teenoor atrasien veroorsaak nie. In 'n afsonderlike ondersoek is die verdraagsaamheid van mieliesaailinge teenoor atrasien ook nie betekenisvol deur hoë P-toediening in die wortelsone of relatief hoë P-konsentrasies in die bogroei van plante beïnvloed nie. Dit blyk dat hoë P-voorsiening en hoë P-vlakke in mieliesaailinge nie die plante se verdraagsaamheid teenoor atrasien beïnvloed nie. Resultate dui daarop dat hoë konsentrasies P, wat in die vorm van kunsmis in die wortelsone van mielies teenwoordig is, nie aanleiding sal gee tot die beskadiging van die gewas deur atrasien nie.



- 3. Met potproewe is aangetoon dat atrasiendrumpelwaarde-konsentrasies in grond vir droëbone, graansorghum, hawer, sojabone en sonneblom van spesie tot spesie en van grond tot grond verskil. Die differensiële gevoeligheid van hierdie gewassoorte behoort meer akkuraat deur wagperiodes, wat na atrasiengebruik in mielies vir gevoelige soorte gestel word, weerspieël te word. Verdere navorsing is nodig om bekende hoeveelhede fitotoksiese atrasienresidue in grond met die reaksie van verskillende spesies in verband te bring, met die oog op beter evaluering van die risiko vir 'n gewassoort waar oordraging van atrasien voorgekom het.
- 4. Die sterkte van verwantskappe tussen geselekteerde grondeienskappe en die bioaktiwiteit en nawerking van atrasien is in 'n totaal van 30 veldproewe by altesaam 10 lokaliteite ondersoek. Die bio-aktiwiteit van atrasien was 35 dae na toediening die beste met die grondeienskappe organiese materiaalinhoud (% C) en P-reversie gekorreleerd. Klei-inhoud en KUV was ook belangrik, maar by laer vlakke van betekenisvolheid. Hierdie bevindings het dié van verskeie vorige ondersoeke, wat geloods is om voorspellers van die aktiwiteit van atrasien te identifiseer, ondersteun.
- 5. Ses maande na onkruiddodertoediening in die proewe wat onder punt 4 bespreek is, het organiese materiaalinhoud, grond-pH en P-reversie onderskeidelik 35%, 19% en 14% van die variasie in bio-aktiwiteit voorspel. Beide klei-inhoud en KUV was swak kriteria van bio-aktiwiteit op daardie stadium. Organiese materiaalinhoud was dominant as voorspeller van beide die korttermyn bio-aktiwiteit (biotoets op dag 0) en langer termyn aktiwiteit (toetsing op dag 182) van atrasien. Aanduidings was dat grond-pH ook 'n belangrike voorspeller van nawerking kon wees. Verskille in verliese tussen



nabygeleë proewe dui daarop dat nawerking van atrasien sterker verband gehou het met die grondeienskappe as met weerstoestande. Resultate dui daarop dat huidige wagperiodes wat vir bepaalde gewasse aanbeveel word, verfyn kan word deur tussen gronde te onderskei op basis van grondeienskappe wat die nawerking van atrasien beïnvloed.

6. Atrasiennawerking na toediening in mielies is vir twee groeiseisoene gemonitor met dieselfde droëboon- en sonneblomkultivars wat hierbo onder punt 3 genoem is. Die doel was om die toepaslikheid van die wagperiode (18 maande) wat vir dié twee gewassoorte aanbeveel word te toets. Oordraging van fitotoksiese atrasienresidue, wat beoordeel is o.g.v. gewasopbrengsverliese, het tussen lokaliteite verskil. Sonneblom was 12 en 24 maande na toediening van atrasien op 'n verskeidenheid grondsoorte meer gevoelig as die droëbone. Dit het die relatiewe gevoeligheid van twee spesies bevestig (sien punt 3). Behalwe by 'n montmorillonietkleigrond is die droëbooncultivar op geeneen van die ander oorwegend kaolinietklei-gronde betekenisvol beskadig nie. Dit word voorgestel dat die wagperiodes vir alle gevoelige spesies verfyn kan word deur differensiële herplant-intervalle op grond- en spesieverskille te baseer.

7. Die invloed van temperatuur en grondwaterinhoud op die nawerking van atrasien is met 'n kleigrond en 'n leemsandgrond ondersoek. Atrasien is bepaal d.m.v. hoëdrukvloeistofchromatografie. Die halfleeftyd van atrasien is ongeveer 60 dae na toediening in die ligte grond bereik, terwyl 70-75% daarvan op dieselfde stadium in die montmorillonietkleigrond oor was. Min tot geen afbraak het in lugdroë grond plaasgevind. Verhoging van die grondwaterinhoud tot by veldkapasiteit het atrasienaf-



braak betekenisvol versnel. Verdere verhoging in die waterinhoud tot by 2x v.k. het nie 'n noemenswaardige invloed gehad nie. Die laagste temperatuurregime het afbraak slegs in die ligte grond betekenisvol vertraag. Grondwaterinhoud en -soort het in hierdie proef 'n groter effek op atrasiennawerking as temperatuur gehad.

- 8. 'n Eenvoudige biotoetstegniek is gebruik om die nawerking van atrasien, wat teen 0.25 kg ab ha¹ op die land toegedien is, in verskillende lae van die profiel van 'n sandkleileemgrond te bepaal. Met dosis-reaksiekurwes is geskat dat 55% van die toegediende atrasien in die 200-300 mm grondlaag, 30 dae na toediening, teenwoordig was. Teen dae 60, 90 en 120 was die persentasies residue in die 200-300 mm grondlaag respektiewelik ongeveer 3%, 2% en 3%. Skattings op dag 120 het daarop gedui dat 2% fitotoksiese residue in die boonste grondlaag teenwoordig was; en 6% in die 300-400 mm laag. Die biotoetstegniek kan toegepas word vir skatting van atrasienresidue in die grondprofiel, veral vir vasstelling van die potensiële risiko vir gevoelige opvolggewasse.
- 9 (a). Die relatief sterk verwantskap tussen grond-pH en atrasiennawerking wat alreeds hierbo gerapporteer is, is weer aangetoon in 'n eksperiment waar atrasienbehandelde grondmonsters op verskillende stadiums gedurende 'n totale inkubasieperiode van 120 dae vir atrasienaktiwiteit getoets is. Basies slegs die pH van die grondmonsters het verskil. Atrasiennawerking het toegeneem met toenemende grond-pH, en sodoende die bevindings van verhoogde atrasienstabiliteit in hoë pH gronde bevestig.
- 9 (b). Dosis-reaksiekurwes is met die toetsplant hawer (cv SWK 001) vir 25 gronde



opgestel vir skatting van die hoeveelhede atrasien, of die fitotoksiese residue daarvan, in elke grond 0, 30, 60, 90, 120 en 150 dae na toediening van 0.2 mg atrasien kg⁻¹. Die tempo van atrasienafbraak in elke grond kon vervolgens voorgestel word met die verwantskap tussen hoeveelheid atrasien en tyd (dae) na dodertoediening. Met hierdie kwadratiese formules is atrasienhalfleeftyd (d.i. aantal dae om 0.1 mg atrasien kg⁻¹ te bereik) vir elke grond geskat. Regressie-analise het getoon dat die kwadraat van grondpH die beste voorspeller van atrasiennawerking is. Organiese materiaalinhoud (% C) was die naasbeste voorspeller. Statisties beoordeel, het slegs (pH)² en % C vir insluiting in 'n meervoudige regressiemodel vir voorspelling van halfleeftyd gekwalifiseer. Dit word voorgestel dat die halfleeftyd van atrasien in grond met die volgende regressie-vergelyking geskat kan word:

$$y = -2.29 + 1.77x_1 + 20.81x_2$$

waar $y = \text{halfleeftyd in dae}; x_1 = [pH(H_2O)]^2; x_2 = \% C$

Resultate wat gedurende hierdie studie gegenereer is behoort 'n bydrae tot kennis en voorspelling van die bio-aktiwiteit en nawerking van atrasien in grond te lewer.



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