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AN OVERVIEW OF ATRAZINE IN THE ESTUARINE ENVIRONMENT

by

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INTRODUCTION

Atrazine (6-chloro-N^2-ethyl-N^4-isopropyl-1,3,5-triazine-2,4-diamine IUPAC or 2-chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine C.A.) is an organic synthetic compound with selective herbicidal properties discovered in 1952 (Esser *et al.*, 1975). It is widely used herbicide for pre- and post-emergence control of grass and broadleaf weeds on agricultural crops mostly maize, sorghum, sugarcane, pineapples and asparagus (Pesticide Manual 1987). Other uses include treatment of turf and more recently in forestry as well as some non-agricultural uses as a soil steriliant, around driveways, railroads, airfields, parking lots and industrial sites (Environment/Agriculture Canada 1987).

The annual usage of atrazine has been estimated in the United States to be more than 40 thousand tonnes per year (Eichers *et al.*, 1978, Berry 1979). Statistics of usage for European countries are not complete in this review and are given only for France, Italy and Greece to be 6000, 300 and 200 tonnes per year respectively (IAEA/FAO/UNEP 1990).

The main environmental concerns for the herbicide atrazine relate to its moderate persistence, to its mode of action as powerful inhibitor of photosynthesis in plants and to its possible toxicity to non-target plants and algae in terrestrial and aquatic environments. Along with its persistence, the movement and mobility of atrazine in the environment has to be a major concern for estuarine and coastal ecosystems.

In most cases atrazine in mammals is rapidly degraded to its metabolites, which are sufficiently water soluble for excretion. As a consequence of efficient excretion, no retention or accumulation of atrazine has been observed in mammals (Esser *et al.*, 975).

Residual concentrations of triazines herbicide are commonly found in continental surface waters in Europe and United States, and frequently exceed the 0.1 $\mu g\ l^{-1}$ admissible concentration of EEC directive in potable drinking water (80/778/EEC).

Triazines are included in the voluntary determinand list of the North Sea Task Force Monitoring Master Plan for study in marine waters. Recent data provide evidence that estuarine waters in Europe are contaminated by atrazine (Ahel *et al.*, 1992, Durand *et al.*, 1992, Allchin and Hamer in prep., Readman *et al.*, submitted, Tronczynski *et al.*, 1992), and some of these data indicate the presence

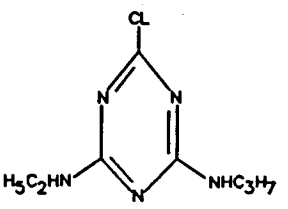
of atrazine in full salinity waters (Tronczynski *et al.*, submitted,). However, the exact extent and frequency of such contamination can not be evaluated on the basis of the data available.

This report represents an bibliographic review focused on an appraisal of the geochemical fate of atrazine in the estuarine environment using as a base recent reviews by Stevenson *et al.*, (1982), Wauchope (1978), Eisler (1989) and Tronczynski (1990).

PHYSICAL AND CHEMICAL PROPERTIES

The physical and chemical properties of atrazine relevant to its environmental behaviour in the aquatic environment are summarized in Table 1.

Table 1.- Physical and chemical properties of atrazine (from Pesticide Manual 1987, Eisler 1989, Kenaga and Goring 1978, Means *et al.*, 1983 and Pereira and Rostad 1990, Jones *et al.*, 1982, Suntio *et al.*, 1988, Wauchope *et al.*, 1992).

Variable	Data
Empirical formula	$C_8H_{14}ClN_5$
Structural formula	
Physical state	Colourless powder
Molecular weight	215.7
Melting point	174°C
Henry's Law constant	3×10^{-4} Pa m^3/mole at 20° C
Vapour pressure	5.7×10^{-8} mm Hg at 10 °C,
	3.0×10^{-7} mm Hg at 20 °C
Water solubility	22 mg/l at 0°C, 33 mg/l at 25°C
Organic carbon partition coefficient (K_{OC}) in :	
Soil	100 to 149
Estuarine sediments	78 to 213
Suspended matter	170 to 2800
Dissolved colloids	1690 to 13600
Octanol Water partition coefficient (K_{OW})	223 to 3468
Half-life in soils	20 to 385 days
Half-life in estuarine sediments	7 to 30 days

The remarkable stability of atrazine is related to its heterocyclic ring, which resembles that of benzene to a some extent. The less pronounced aromatic character of the s-triazine structure is explained by the greater electronegativity of nitrogen atoms and the positive charge on the carbon atoms.

Aqueous solubility and *n*-octanol – water partition coefficients are related to one other, and are useful parameters for predicting the partitioning of pesticides in aquatic environments (Kenaga and Goring 1978). These and other properties of atrazine were used to calculate its potential distribution between non-living (air, water, soil, sediments, suspended solids) and living (aquatic biomass, terrestrial plants) environmental compartments in a model ecosystem (Bacci et al. 1989). From this model it appears that transport of atrazine occurs essentially in water, and that water is the major reservoir in the aquatic environment.

ANALYTICAL METHODOLOGY AND PROCEDURES

Analytical methods for analysis of pesticides in different environmental matrices have been recently reviewed by Chau and Afghan (1982), Barcelo (1991), Sherma (1991). As a consequence of the world-wide use of *s*-triazine herbicides a variety of analytical techniques have been developed, and the determination of these agrochemicals in the natural environment is relatively well documented (Pressley and Longbottom 1982, Pereira and Rostad 1990, Battista *et al.*,1989, Thurman *et al.*, 1990, Tronczynski *et al.*1992,in press, Readman *et al.*, submitted, Ahel *et al.*, 1992). In this section an overview of analytical procedures for atrazine analysis will be outlined together with a critical evaluation of the suitability of these techniques for the analysis of estuarine and coastal waters. Many of these methods were developed for multiresidue measurements of pesticides and only their relevance to atrazine determination is considered here, not their inherent advantages and disadvantages for the analysis of a wide range of pesticides. Furthermore, although triazines have been reported in all compartments of the natural environment (Wauchope 1978, Chau and Afghan 1982, Glotfelty *et al.*,1984), water is the main matrice of concern. Therefore in this short outline only the analysis of water and sediment samples is discussed, and readers interested in biota analysis (fish and plants) are referred to more extensive analytical reviews (Sherma 1991, Chau and Afghan 1982).

GENERAL

Quality control, conducted by rigorous implementation of intralaboratory QC protocols, and by collaborative studies, is essential in order to establish the precision and accuracy of pesticides analysis. Interlaboratory studies are particularly necessary as certified reference materials for atrazine are not currently available. Lyophilized water samples prepared for pesticide intercomparison exercises have been analysed by a few European laboratories and the results of these analyses will be compiled soon (Dr. Barcelo, pers. comm.).

The quantitative determination of herbicides in the marine environment requires a very good analytical method with sensitivity in the low ng l^{-1} concentration range as well as good selectivity. Generally, the analytical scheme for determination of triazines is not different from that commonly accepted for trace organic contaminant analysis i.e. including appropriate sampling equipment; sample transport, preservation and filtration; extraction; extract concentration; cleanup; and detection with positive identification and quantification.

ISOLATION AND ENRICHMENT

A wide variety of isolation or enrichment procedures can be used for the extraction of atrazine from water samples. The conventional approach is liquid-liquid extraction (LLE) with an organic solvent, based on the partitioning of the analyte into the solvent phase (Chau and Afghan 1982).

In general, atrazine is easily extracted into organic solvents not miscible with water, and the choice of the solvent for LLE is not critical. Most of the recent reports on dissolved triazines were using dichloromethane for LLE, and showed good recoveries (80 to 100%) of these compounds (Pereira *et al.*, 1990, Barcelo *et al.*, 1991). The extraction can be enhanced by using mixed solvents or a sequence of different solvents, when more polar and less hydrophobic metabolites (like N- dealkylated degradation products) of atrazine are to be analyzed (Durand and Barcelo 1989). The highest quality solvents (such as for trace analysis or pesticide – grade) should always be used for extraction as the analytical blanks must be minimised for the measurement of concentrations in the low ng l^{-1} range.

The filtration of water samples is necessary, despite the fact that the relative contribution of particulate atrazine is less than 1% of the total, as the extraction efficiency may be influenced by the presence of large amount of solid particles, and substances extracted from the suspended matter may interfere with subsequent chromatographic analysis. The water samples should be fortified with an appropriate amount of internal standard surrogate for a measure of the extraction efficiency. The surrogate can be one of the other *s*-triazine herbicides which is neither in use nor sold in the region. Finally, the influence of the high gradients of the ionic strength and other physicochemical variables in estuarine water samples on the recoveries of triazines by LLE should be carefully examined. However these variations in natural conditions are not expected to significantly influence atrazine recovery.

Although LLE remains a widely recognized technique for trace organic contaminants analysis it has proved to have many shortcomings (cost, time consuming, use of large volumes of toxic and inflammable solvents, cumbersome utilisation on – board ship, possible contamination of samples and difficult automation and storage of the samples). For these reasons solid – phase – extraction (SPE) or liquid – solid – extraction (LSE) have been recently developed and these techniques are rapidly becoming fully accepted for the enrichment of pesticides (Frei *et al.*, 1986, Nielen 1988, Lopez–Avia *et al.*, 1985). SPE is based on the liquid solid partition of the analyte, and yields efficient retention for a given sample volume. The solid sorbent offers combined sampling, enrichment, cleanup, sample storage, field use, ease of automation and on – line desorption. Clearly this technique has a promising future as a whole for the analysis of the contaminants dissolved in water and will continue to develop in parallel with the progress in research on the chemistry of sorbents.

Dissolved atrazine can be retained by wide variety of sorbents such as C_8 or C_{18} bonded silica (Bagnati *et al.*, 1988, Mills and Thurman 1992, Mills *et al.*, 1993), graphitized black carbon (GCB) (Di Corcia *et al*, 1987, Di Corcia and Marchetti 1991), Amberlite XAD resins (Galassi *et al.*, 1988, Biziuk and Tronczynski submitted) and PLRP–S or PRP–1 copolymers (Subra *et al.*, 1989, Hennion *et al.*, 1990, Bagheri *et al.*, 1992). Samples from a just a few millilitres to several liters of water can be passed through a bed of sorbent. One parameter to control is the breakthrough volume, which depends on the quantity of sorbent and its retention capacity, and on other factors such as flow – rate and pH of the sample. Typically, a high degree of deactivation of sorbent and strong polar eluents must be used in order to ensure quantitative desorption of the triazine herbicides (Lee and Stokker 1986). Elution is accomplished with methanol, acetonitrile, methylene chloride, ethyl acetate or mixtures of different polarity solvents. Selective desorption of the analyte can be achieved by careful choice of the eluting solvent or by the use of mixed – mode resins thereby introducing a cleanup step by the removal of organic matter impurities (Ahel *et al.*, 1992, Mills and Thurman 1992).

Another advantage of the SPE technique is the ease of development of on – line procedures consisting of enrichment, desorption and chromatographic detection in a single run by direct connection, through a switching valve, of the sorbent cartridge with a chromatographic system (Slobodnik *et al.*,1992). This analytical set – up can be fully automated, yielding low detection limits and a very high through – put of samples. Hence it is particularly attractive for monitoring programmes. The main drawbacks of the on – line SPE technique is that it allows only one analysis per sample, and that it most easily interface with HPLC which is not analytical technique of choice for triazines. Nevertheless the SPE technique gains in popularity and in recognition and can be merged in a fully validated method for pesticides preconcentration.

There has been relatively little work undertaken on analysis of the sediment for atrazine, and on effective extraction techniques. Many factors affect the recovery of triazines from sediments. The evidence for complex physical and chemical sorption mechanisms and the identity, nature and properties of non extractable triazine residues in soils, raise analytical problems and pose a challenge to the analytical chemist (IUPAC 1984). Therefore, the present discussion is limited only to basic considerations concerning the extraction of atrazine from sediments.

Freeze – drying is a common method for the preparation of sediment samples. One report indicated that freeze – drying before extraction did not improve the recovery of pesticides compared with wet extraction, but interference from other co–extracted materials increased considerably (Muir and Baker 1976, Kjolholt 1985). It is apparent that hot methanol, methanol – water, acetone, acetonitrile and water are efficient solvent systems for the extraction of triazine residues (Mills and Thurman 1992).

Extraction can be accomplished by Soxhlet or sonication of sediment samples. More severe methods which facilitate the extraction of the bonded fraction of pesticides (e.g.: alkaline or acidic digestion) are not recommended because of degradation of analytes. Soft extraction techniques (such as supercritical fluid extraction (SFE) or mixed – mode resins SPE) have been used successfully for the isolation of triazines from soil and sediment samples (Mills and Thurman 1992, Snyder *et al.,* 1992).

CLEANUP

Cleanup procedures are rarely essential for extracts of water samples , because of the common use of the selective gas chromatographic detectors for the determination of triazines. Furthermore the use of SPE techniques allows the introduction of a cleanup step into desorption phase. Generally, cleanup methods for the triazines extracts from sediment samples are based on the use of column chromatography with silica gel, alumina or Florisil and gel – permeation chromatography (GPC). Several authors have however reported that simple solvent partitioning is sufficient (Chau and Afghan 1982, Pressley and Longbottom 1982, Durand *et al.*, 1989).

ANALYTICAL TECHNIQUES

Two main analytical techniques are used for the analysis of triazine residues: high resolution gas chromatography (HRGC) and high performance liquid chromatography (HPLC). Both techniques may be connected with a wide variety of detectors. For GC the most common detectors used for detection of triazines are: nitrogen – phosphorous detector (NPD), (Ahel *et al.,* 1992, Durand *et al* 1992, Tronczynski *et al* submitted), electron capture detector (ECD), and mass spectrometers (usually quadrupole and ion trap – ITD), (Pereira and Rostad 1990, Durand and Barcelo 1991, Tronczynski *et al* 1993, Bagheri *et al* 1992). Liquid chromatography systems may be coupled with an ultraviolet detector (Battista *et al.,* 1989, Durand *et al.,*1992) or to a mass spectrometric detector through recently developed interfaces such as thermospray (TSP) (Voyksner and Haney 1985, Bellar and Budde 1988), particle beam (PB) (Miles *et al.,* 1992) or atmospheric– pressure (APCI) (Doerge and Bajic 1992). Nevertheless the HPLC techniques will not be a method of choice for atrazine determination unless more polar, thermally labile or low volatility metabolites and other pesticides have also to be analysed. The LC could also be recommended if the on–line SPE technique is to be used.

Gas chromatography is the most powerful and commonly used technique for the determination of triazine residues in environmental samples. The NPD detector has been widely used and yields good sensitivity (< 10 pg of atrazine injected), allowing the determination of concentrations in the low ng l^{-1} range in estuarine samples (Ahel *et al.,* 1992). However, recent investigations indicate that the response of the NPD detector may not be as linear as was originally accepted (Philpott *et al.,* 1991). This necessitates careful calibration. The use of dual capillary columns should be recommended in gas chromatographic analysis of triazines, thus optimising the separation and identification of the compounds, and possibly lowering detection limits.

Gas chromatography coupled to a mass spectrometer (commonly used in the electron impact EI mode) is well established for the identification and confirmation of triazines as well as their quantification. Very good sensitivity in selected ion monitoring mode (a few picograms injected at S/N ratio of 3 to 1) has been reported (Bagheri *et al;,* 1992). Of the various ionization modes, EI was found to be more sensitive than either positive chemical ionisation (PCI) or negative chemical ionisation (NCI) (Stan and Bockhorn 1991, Rostad *et al.,* 1989).

A few reports have demonstrated the very good sensitivity (50 pg at S/N 10 to 1) and reproducibility of ion trap detectors used in conjunction with gas chromatography for triazine studies in natural water samples (Periera and Rostad 1991, Ahel *et al.,* 1992).

In conclusion, GC with a selective nitrogen – phosphorous detector will be the analytical technique of choice for most laboratories due to the low cost of equipment and relatively simple operation. However, the use of bench – top quadrupole or ion–trap mass detectors will in addition provide unambiguous identification of the analyte.

PATHWAYS FOR ENTERING THE ESTUARINE ENVIRONMENT

The environmental transport of atrazine to estuaries poses two major research questions i) What are the amounts of atrazine in runoff from agriculture fields entering surface and subsurface waters ii) What are the dispersion, dilution and degradation rates of atrazine in surface waters and estuaries.

RUNOFF LOSSES

The majority of atrazine loss via surface runoff occurs immediately following application and during rainstorm events (Wauchope 1978, Triplett *et al.* 1978, Muir *et al.*, 1978, Frank *et al.* 1979, Wu *et al.*, 1983). Atrazine losses were found to vary strongly, from 0.1 to 18 % of the amount applied on agricultural areas with different drainage characteristics. In practice these losses are closely correlated with environmental and meteorological conditions. In addition, several soil factors influence the losses of atrazine. Frank and Sirons (1985) found a good correlation between the percentage of clay, and losses of atrazine in surface runoff, ranging from a low loss of 0.4 g/ha (or 0.33 % applied) from sandy soils, a medium loss of 1.8 g/ha (or 0.60 % applied) from loams, and a high loss of 4.0 g/ha (or 1.93 % applied) from clay soils. However, this study indicate also that sandy soil may lose trapped atrazine later in the season with the peak concentrations associated with base flow in the soil.

Leaching is not a major pathway for loss of atrazine (Helling 1970), although low ppb levels have been detected in ground water in sandy soils. Transport in the vapour phase is not an important pathway, since the triazine herbicides are relatively non-volatile. They have however, been detected in rainwater in a few recent studies (Wu, 1981; Richards *et al.*, 1987, Scharf *et al.*, 1992).

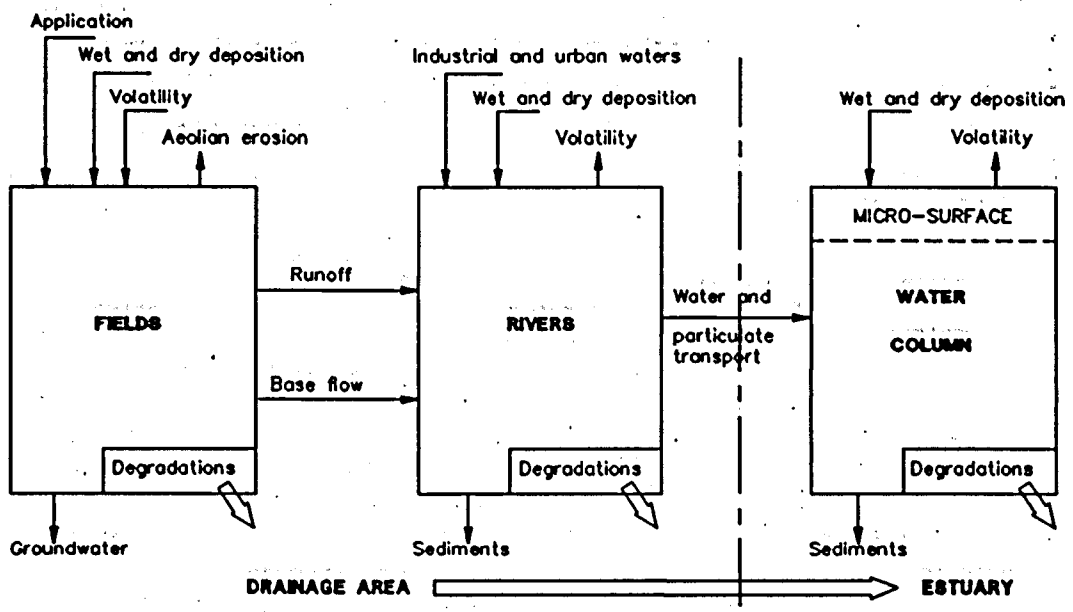


Figure 1 – Schematic flows of atrazine from agricultural fields to estuarine waters.

It is apparent in reviewing long term loss patterns that single storm losses can be very important in determining the inputs of atrazine into receiving waters, including estuaries. A schematic illustration of atrazine movement from agricultural fields to rivers and estuaries is shown in Figure 1 (adapted from Stevenson *et al.* 1982). In order to assess the atrazine loading rates we also need information on its the prevailing transport patterns, and on the environmental rate constants of degradation processes. The weakness of these estimates lies in our ability to establish or predict environmental rate constants, which moreover vary between terrestrial, freshwater and estuarine ecosystems.

TRANSPORT PATTERNS

The transport of atrazine in estuarine waters is mostly in the water phase, exhibiting nonconservative mixing and dilution. (Means *et al.*, 1983 ; Stevenson *et al.*, 1982 ; Wu, 1980; Newby *et al.*, 1978). The nonconservative distribution of atrazine can be inferred from concentrations in water of the Susquehanna River mouth, determined over the salinity range from 2 to 15 %. (Newby *et al.*, 1978) – (Fig. 2 from Stevenson *et al.*, 1982). The discrepancy between a theoretical dilution curve of expected and measured atrazine concentrations indicates large losses of atrazine which occur in the mixing zone of the estuary. These results are also consistent with the results of Means *et al.* (1983) in area of Chesapeake Bay, and of Wu (1981) in Rhode River estuary.

However, these data are not consistent with recent study of chlorotriazine herbicides in estuarine waters in Europe (Ahel *et al.*, 1992 Tronczynski *et al.*, submitted). These data indicate apparent conservative mixing of atrazine in the estuaries studied. Peak concentrations are related to the pulse inputs caused by application on agriculture land or to the hydrological events and hydrodynamic conditions (Tronczynski *et al.*, submitted). The abrupt increase of concentrations after spreading of herbicides is followed by "diffusive-like" contamination (Tronczynski *et al.*, submitted). It appears that some discrepancies in scarce field data exist, and there are other possible factors which may account in part for the patchiness of atrazine levels in estuaries.

The effect of dilution factors alone on atrazine concentration may be useful in predicting whether other removal processes (such as adsorption or degradation) from water are needed to reach low or undetectable levels in large water bodies such as estuaries.

The absence of detectable residues of atrazine in estuarine sediments and suspended particulates, in spite of its known affinity for adsorption, was explained either in terms of relatively rapid degradation of this herbicide in estuarine sediments (Jones *et al.*, 1982), or by the increased pH in sediments promoting atrazine retention in the dissolved phase (Kells *et al.*, 1980). Furthermore, high KDOC values of atrazine for dissolved colloidal matter reduces the bonding of atrazine with suspended matter and probably increases the amount of atrazine that will remain in the water phase (Means *et al.*, 1983; Means and Wijayaratne 1982). Rapid adsorption–desorption kinetics develop a rapid equilibrium (Wauchope and Meyers, 1985) suggesting that atrazine bound to soil particles, upon entering the surface waters with the lower suspended solids concentrations, would rapidly be desorbed, and subsequently a new equilibrium would be established.

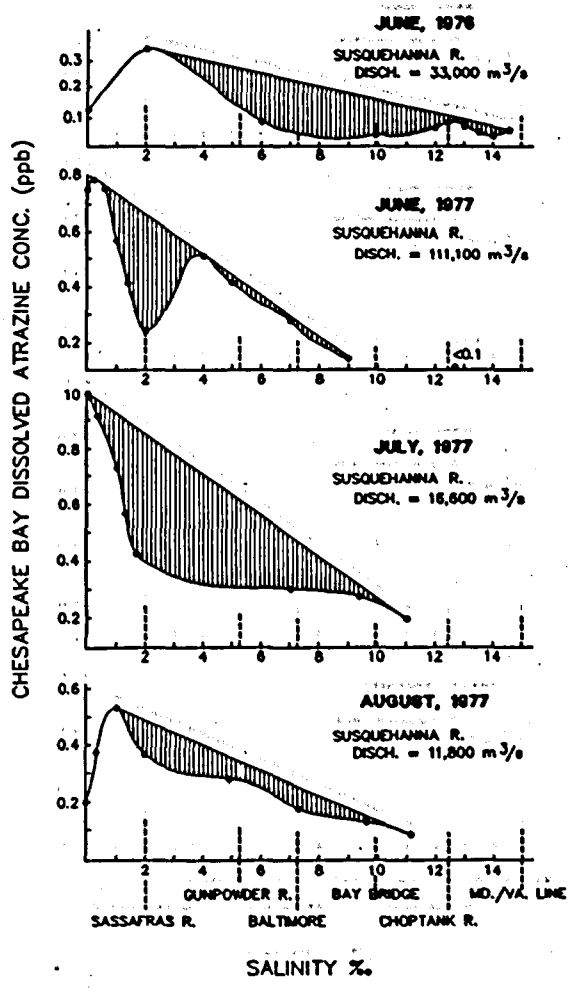


Figure 2.– Concentration of atrazine at the mouth of the Susquehanna River, Chesapeake Bay estuary (from Stevenson *et al.* 1982).

Colloidal dissolved organic matter from an estuarine environment was found to have 10 to 35 times higher adsorption capacity for atrazine than sediment or soil organic matter (Means *et al.*, 1983). The presence of colloids in estuarine waters was postulated to be an important factor affecting the transport and distribution of atrazine in aquatic systems.

The presence of atrazine in rainwater has recently been reported (Wu, 1981; Richards *et al.*, 1987). The atmospheric residence time of moderately stable pollutants, like atrazine, would suggest the possibility of its remote atmospheric dispersal. In the same study, Wu (1981) demonstrated atrazine enrichment in the surface microlayer of estuaries relative to the underlying water.

PERSISTENCE AND DEGRADATION

Atrazine may be removed from the aquatic environment by both chemical and microbial degradation. Atrazine degradation proceeds via abiotic hydrolysis in estuarine sediments (Wu and Fox 1980, Jones et al, 1982). The occurrence of the corresponding hydroxy-derivatives as major short-term degradation products in sterilized soil is clear evidence for the participation of non biological mechanism in atrazine degradation (Armstrong et al., 1967). The absence of a lag phase in the degradation of triazines in soil is also indicative of chemical hydrolysis. Atrazine degradation was much more rapid in estuarine sediments (half-life from 15 to 20 days) than in agricultural soil (half-life from 330 and 385 days).

Microbial degradation occurs primarily via N-dealkylation to yield desethyl- or desisopropyl-atrazine. These intermediates preserve partial phytocidal activity (Esser *et al.*, 1975). The ease of cleavage of alkyl groups by micro-organisms decreases in the sequence ethyl, isopropyl, then larger and more branched alkyl groups. The minor processes of microbial degradation of atrazine are deamination, dehalogenation and hydroxylation. In recent studies in the Mississippi River, the ratios of desethylatrazine to atrazine concentrations were used as an index of biodegradation of atrazine (Pereira and Rostad, 1990).

ENVIRONMENTAL CONCENTRATIONS

Recent data provide evidence that estuarine waters in Europe are contaminated by atrazine (Ahel *et al.*, 1992, Durand *et al.*, 1992, Allchin and Hamer in prep., Readman *et al.*, submitted, Tronczynski *et al.*, 1993, Tronczynski *et al.*, submitted). Some of these data indicate the presence of atrazine in full salinity waters (Tronczynski *et al.*, submitted, Allchin and Hamer in prep.). The exact extent and frequency of this contamination can not be evaluated on the basis of the available data. This is in contrast to voluminous literature on atrazine concentrations in surface waters (Stevenson *et al.*, 1982 ; Eisler, 1989). Atrazine estuarine water concentrations are summarized in the Table 2.

In general, atrazine concentrations range from < 0.001 μg/l to < 1 μg/l in estuarine waters and from 0.1 to 30 μg/l in surface and subsurface fresh water systems (Refs. in Table 2). The Concentrations exceeding these ranges are generally associated with runoff events. Moreover their occurrence is of short duration and mostly derive from local diffuse or point agricultural sources, and it is obvious that these concentrations are highly transient.

TOXICITY TO ESTUARINE AQUATIC ORGANISMS

Extensive toxicity testing using a variety of aquatic organisms has been conducted with atrazine (EPA 1987, Eisler 1989, Stevenson *et al.*, 1982). and the interested reader is referred to these reviews.

Briefly, concern over atrazine's mode of action in terrestrial plants (the inhibition of photosynthesis of Hill reaction i.e. the evolution of oxygen from water in the presence of chloroplast) has led to numerous studies with both macro and microscopic algae. The rationale for these studies was firstly that atrazine levels in natural waters would have a selective action for certain species and may create monospecific algal blooms and secondly that effects on primary producers of the food chain may have profound effects in higher trophic levels (Larsen *et al.*, 1986).

In general, the effective concentrations (EC50) of atrazine for different algal species are in the range from 60 mg/l to 460 mg/l for different of exposure times. The most sensitive species were *Chlamydomonas sp., Monochrysis lutheri, Cyclotella nana* in a 72 hour test, and the most resistant was

Navicula inserta (EPA 1987). The triazines are low in acute toxicity, and atrazine appears to be nonmutagenic and nonteratogenic. However, there is not sufficient data to draw unequivocal conclusions regarding its mutagenic, teratogenic and carcinogenic actions (Donna *et al.*, 1981).

Table 2.– Atrazine Estuarine water concentrations ($\mu g/l$)

AREA WATER ORIGIN	CONCENTRATION ($\mu g/l$)	REFERENCE
Chesapeake Bay (US)		
Runoff waters	480.0	Forney, 1980
Susquehanna estuary	0.3 – 1.1	Stevenson *et al.*, 1982
Horn Point and tributaries	0.1 – 46.0	Kemp *et al.*, 1985
Choptank estuary with runoff event	0.0 – 9.3	Kemp *et al.*, 1985
Chesapeake Bay	0.0 – 1.1	Means *et al.*, 1983
Maryland (US)		
Wye river	3.0 – 15.0	Glotfelty *et al.*, 1984
Rhode River (US)		
Water column	0.006 – 0.19	Wu, 1981
Microsurface layer	0.010 – 3.3	"
Rainwater	max. 2.2	"
Tamar estuary (UK)	0.006 – 0.04	Ahel *et al.*, 1992
Humber estuary (UK)	0.040 – 0.170	Apte and Rogers 1993
Coastal waters (UK)	< 0.001 – 0.067	Allchin and Hamer (in prep.)
Thermaikos Gulf (Greece)	< 0.050 – 0.150	Readman *et al.*, submitted
Amvrakikos Gulf (Greece)	< 0.050 – 0.800	"
Northern Adriatic (Italy)	< 0.003 – 0.018	"
Ebro Delta (Spain)	<0.001 – 0.057	"
Rhone Delta (France)	0.017 – 0.386	"
Ebro Delta (Spain)	< 0.005 –0.280	Durand *et al.*, 1992
Rhône Delta (France)	0.01 – 0.060	Tronczynski *et al.*, 1993
Coastal Atlantic waters (France)	0.005 – 0.038	Munschy *et al.*, 1993
Charente estuary (France)	0.032 – 0.287	Munschy *et al.*, 1993
Seine estuary (France)	0.005 – 0.430	Tronczynski (in prep.)

"<" values indicate the detection limits of the analytical techniques

REFERENCES

Ahel M., K. M. Evans, T.W. Fileman and R. F. C. Mantoura, 1992. *Anal. Chim. Acta* 268, 195–204.

Allchin C. R. and R. Hamer (in prep.) To be submitted to *Marine Pollution Bulletin*.

Armstrong D. E., G. Chester and R. F. Harris, 1967. *Soil Sci. Soc. Am. Proc.*, 31, 61–66.

Apte S.C., and H.R. Rogers, 1993. *Sci. Total Environ.*, 132, 313–325.

Bacci E., A. Renzoni, C. Gaggi, D. Calmari, A. Franchi, M. Vighi and A. Severi, 1989. *Agric. Ecosys. Env.*, 27, 513–522.

Bagheri H., J. J. Vrelus, R. T. Ghijsen U. A. Th. Brinkman, 1992. *Chromatographia* 34, 5–14.

Bagnati R., E. Benfenati, E. Davoli, R. Fanelli, 1988, *Chemosphere*, 17, 59–65.

Barcelo D., 1991. *Analyst*, 116, 681–689.

Barcelo D., G. Durand and J. Albaiges, 1991. In: *Oragnic Micropllutants in the Aquatic Environment*, G. Angeletti and A. Bjorseth eds., Kluwer, Dordrecht, 132–141.

Berry, J. H., 1979. In : *Pesticides role in agriculture, Health and environment*, T. J. Sheets and D. Pimental eds. Humana Press, Clifton, N.J.

Battista M., A. Di Corcia and M. Marchetti, *Anal. Chem.*, 1989. 61, 935–939.

Bellar T. A. and W. L. Budde 1988, *Anal. Chem.*, 60, 2076.

Biziuk M., and J. Tronczynski Submitted to *Int. J. Environ. Anal. Chem.*

Chau, A. S. Y., and B. K. Afghan , 1982. In: *Analysis of pesticides in water*. v. III CRC Press, Inc.

Doerge D. R. and S. Bajic 1992. *Rap. Comm. Mass Spec.*, 6, 663–666.

Di Corcia A., M. Marchetti, R. Samperi. 1987. *J. Chromatogr.*, 405, 357–363.

Di Corcia A., and M. Marchetti 1991., *Anal. Chem.*, 63, 580–585.

Donna, A., P. G. Betta, F. Gagliardi, G. F. Ghiazza, M. Gallareto and V. Gabutto, 1981. *Pathologica*, 73, 707–721.

Durand G. and D. Barcelo, 1989 *Toxicol. Environ. Chem.*, 25, 1–11.

Durand G., R. Forteza and D. Barcelo, 1989. *Chromatographia*, 28, 597–604.

Durand G. and D. Barcelo 1991. *Anal. Chim. Acta*, 243, 259–271.

Durand G., V. Bouvot and D. Barcelo, 1992. *J. Chromatogr.*, 607, 319–327.

Eichers, T. R., P. Andrilenas and T. W. Anderson, 1978. U. S. Department of Agriculture *Report N° 418*, Washington, D. C., 58 p.

Eisler R., 1989. *Contaminant Hazand Reviews*. Report n° 18. Fish and Wildlife Service. U. S. Dep. of the Interior 53 p.

Environment Canda/Agriculture Canada, 1987. Pesticide registrant survey 1986 Report. January 1987.

EPA US, 1987. U. S. Environmental Protection Agency, Washington, D. C EPA/600/8–87 : 017.

Esser H. O., G. Dupuis, E. Ebert, Ch. Vogel and G. J. Marco, 1975. In : *Herbicides chemistry, degradation, and mode of actions.* eds. P. C. Kearney and D. D. Kaufman 2end edition Vol. 1, 129–187.

Forney D. R., 1980. M. S. Thesis. Auburn University, Alabana, 76 p. (in: Eisler, 1989).

Frank R. and G. J. Sirons, 1979. *Sci. Total Environ.* 12, 223 – 239.

Frank R. and G. J. Sirons, 1985. *Bull. Environ. Contam. Toxicol.*, 34, 541 – 548.

Frei R., M. W. F. Nielen, and U. A. Th. Brinkman, 1986. *Int. J. Environ. Anal. Chem.*, 25, 3.

Galassi S., A. De Paolis, A. Berri and L. Guzzela 1988. *Acqua Aria*, 3, 327–331.

Glotfelty D. E., A. W. Taylor, A. R. Isensee, J. Jersey and S. Glmn, 1984. *J. Environ. Qual.*, 13, 115 – 121.

Helling C. S. 1970. *Res. Rev.*, 32, 287.

Hennion M–C., P. Subra, R. Rosset, J. Lámacq, P. Scribe and A. Saliot 1990. *Intern. J. Environ. Anal. Chem.*, 42, 15–33.

IAEA/FAO/UNEP/MED/POL.– Workshop on the assessment of pollution by herbicides and fungicides 1990, Meeting Report.

IUPAC Commision on pesticide chemistry. 1984. Pure Appl. Chem., 56, 945–956.

Jones, T. W., W. M. Kemp, J. C. Stevenson and J. C. Means, 1982. *J. Environ. Qual.* 11 : 632 – 638.

Kells, J. J., C. E. Rieck, R. L. Blevins and W. M. Muir, 1980. *Weed Sci.* 28, 101–104.

Kemp W. M., W. R. Boynton, J. J. Cunningham, J. C. Stevenson, T. W. Jones and J. C. Means, 1985. *Marine Environ. Res.* 16, 255 – 280.

Kenaga E.E. and C. A. I. Goring, 1978. *Aquatic toxicology, ASTM STP* 707, J. G. Eaton, P. R. Parish et A. C. Hendricks, Eds, 78 – 115.

Kjolholt J. 1985. *J. Chromatogr.*, 325, 231–238.

Larsen, D. P., F. de Noyelles Jr, F. Stay and T. Shiroyama, 1986. *Environ. Toxicol. Chem.*, 5, 179–190.

Lee H–B., Y.D. Stokker, 1986. *J. Assoc. off Anal. Chem.*, 69, 568–572.

Lopez–Avia V., P. Hirata, S. Kraska, M. Flanagan, J.H.. Taylor Jr. and S.C. Hern, 1985 *Anal. Chem.*, 57, 2797–2801.

Means J. C., S. G. Wood, J. J. Hassett et W. L. Banwart, 1980. *Environ. Sci. Technol.* 14, 1524 – 1528.

Means J. C. and R. D. Wijayaratne 1982. *Science*, 215, 968–970.

Means J. C., R. D. Wijayaratne et W. R. Boynton, 1983. *Can. J. Fish Aquat. Sci.* 40 (suppl. 2), 337 – 345.

Miles C. J., D.R. Doerge and S. Bajic 1992. *Arch. Env. Contam. Toxicol.*, 22, 247.

Mills M. S. and E. M. Thurman, 1992. *Anal. Chem.*, 64, 1985–1990.

Mills M. S., E.M. Thurman and M.J. Pedersen 1993. *J. Chromatogr.*, 629, 11–21.

Muir D. S. G., J. Y. Yoo and B. E. Baker 1978. *Arch. Environ. Contam. Toxicol.* 7, 221–235.

Muir D.C. and B.E. Baker 1976. *J. Agr. Food Chem.* 24, 122.

Munschy C, Tronczynski J., Durand G., and Barcelo D. (1993) Abstract *4th Workshop on Chemistry and Fate of Modern Pesticides and Related Pollutants*, IAEAC, Prague, September 8–10, 1993.

Newby L.C., R.A. Kahrs, K. Adams and M. Szoolics 1978.Ciba–Geigi Corp., Greensboro, NC. 25 pp.

Nielen M. W. F., 1988. In: *Selective on – line pre – column sample handling and trace enrichment in liquid chromatography*. eds Frei R. W. and Zech K., Elsevier, Amsterdam, J. Chromatogr. Libr., 38A, ch.1.

Pereira E. W. and C. E. Rostad, 1990. *Environ. Sci. Technol.* 24, 1400–1406.

Pereira W.E., C. Rostad and T.J. Leiker, 1990. *Anal. Chim. Acta*, 228, 69–75

Pesticide manual (The). *A world compendiuim*. 1987 8th edition eds.: Ch. R. Worthing and S. B. Walker, BCPC – British Crop Protection Council. 1081 p.

Philpott M. F., M. J. Vander Merwe 1991. *Chromatographia*, 31, 500–504.

Pressley T. A., J. E. Longbottom, 1982. Method 619, US EPA, Cincinatti, OH, 1–23.

Readman J.W., T.A. Albanis, D. Barcelo, S.Galassi, J.Tronczynski and G.P. Gabrielides (submitted) *Mar. Pol. Bull.*

Richards R. P., J. W. Kramer, D. B. Baker and K. A. Krieger, 1987. *Nature*, 327, 129 – 131.

Rostad C. E., W. E. Periera, T.J. Leiker 1989. *Biomed. environ. Mass Spectrometry*, 18, 820.

Scharf J., R. Wiesiollek and K. Bachman 1992. *Fresenius J. Anal. Chem.*, 342, 813–816.

Sherma J., 1991. *Anal. Chem.*, 63, 118R–130R

Slobodnik J., E. R. Brouwer, R. B. Geerdink, W. H. Mulder, H. Lingeman and U. A. Th. Brinkman, 1992. *Anal. Chim. Acta*, 268, 55-65.

Snyder J. L., R.L. Grob, M-E. McNally and T.S. Oostdyk. 1992. *Anal Chem.*, 64, 1940-1946.

Stan H. J., A. Bochorn 1991. *Anal. Chem.*, 339, 158.

Stevenson J. C., T. W. Jones, W. M. Kemp, N. R. Boyton and J. C. Means, 1982. In : *Agrichemicals and estuarine productivity*. J. O. Costolow, L. E. Cronin, T. B. Duke et W. Mc Clellan (Eds) John Wiley & Sons Ltd. N. Y.

Subra P., Hennion M. C., Rosset R., Frei R. W., 1989. *Intern. J. Environ. Anal. Chem.*, 37, 45 - 62.

Suntio L.R., W. Y. Shiu, D. Mackay, J.N. Seiber and D. Glotfelty 1988. *Rev. Environ. Contam. Toxicol.*, 103, 1-59.

Thurman E.M., M. Meyer, M. Pomes, C.A. Perry and A.P. Schwab, 1990. *Anal. Chem.*, 62, 2043-2048.

Triplett G. B. (JR), B. J. Conner and W. M. Edwards, 1978. *J. Environ. Qual.* 7, 77-84.

Tronczynski J., 1990. IFREMER, DRO-90-05-MR, 39 p.

Tronczynski J., Munschy C., Durand G and Barcelo D. (1993). *Sci.Total Environ.* 132, 327-337.

Tronczynski J., Munschy C. and Pont D. (1993). Abstract *4th Workshop on Chemistry and Fate of Modern Pesticides and Related Pollutants*, IAEAC, Prague, September 8-10, submitted to Intern. J. Environ. Anal. Chem.

Voyksner R. D. and C. A. Haney 1985. *Anal Chem.*, 57, 991.

Wauchope R. D., 1978. *J. Environ. Qual.*, 7, 459-472.

Wauchope R. D. and R. S. Meyers, 1985. *J. Environ. Qual.*, 14, 132 - 136.

Wauchope R. D., T. M. Buttler, A. G. Hornsby, P.W. Augustijn Beckers and J. P. Burt 1992. *Rev. Environ. Contam. Toxicol.*, 123, 1-155.

Wu T. L. and B. M. Fox, 1980. Proc. Northeast Weed. Sci. Soc. 34, 147 - 154.

Wu T. L., 1980. *J. Environ. Qual.* 9, 459 - 465.

Wu T. L., 1981. *Water, Air and Soil Pollution*, 15, 173 - 184.

Wu T. L., D. L. Correll et H. E. H. Remenapp, 1983. *J. Environ. Qual.*, 12, 330 - 336.