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Coastal Water Contamination from a Triazine Herbicide Used in Antifouling Paints

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Introduction

Research into the environmental distribution and effects of biocides added to marine paints has, to date, been focused on the antifouling agent tributyltin (TBT). It has been estimated that in Arcachon Bay (France) alone, the use of TBT provoked a loss in revenue of 147 million U.S. dollars through reduced oyster production (1). Its use has subsequently been severely restricted internationally (1, 2), and TBT has largely been replaced by copper-based substitutes. In addition to these biocides (which are added primarily to control aquatic animals), herbicides are also frequently added to inhibit primary colonization of hull surfaces by micro-algae and subsequent growth of seaweeds. Environmental contamination by these compounds has not, to date, been reported. 2-Methylthio-4-*tert*-butylamino-6-cyclopropylamino-*s*-triazine (trade name: IRGAROL 1051) is an effective herbicidal additive, and analytical methods were developed within our laboratory to afford quantification of this compound in environmental waters in order to investigate coastal contamination.

Materials and Methods

Subsurface (20 cm depth) coastal water samples were collected in precleaned glass bottles from a selection of locations on the Côte d'Azur (Figure 1). Samples (taken between June 3–21, 1992) were maintained in a cool, dark environment and were extracted within 3 days of collection. Aliquots (1.00 L) were spiked with an internal standard (chlorthion; 50 ng) and, using a peristaltic pump, were drawn through a glass fiber filter (0.7- μ m pore size) followed by a C₁₈-bonded silica cartridge (1 g; Supelco R; washed with 1 mL of methanol and 1 mL of ethyl acetate and then activated with 4 mL of methanol followed by 4 mL of double-distilled water). The flow of the sample was adjusted to average 15 mL min⁻¹. Following extraction, the cartridges were eluted with 4 mL of ethyl acetate from

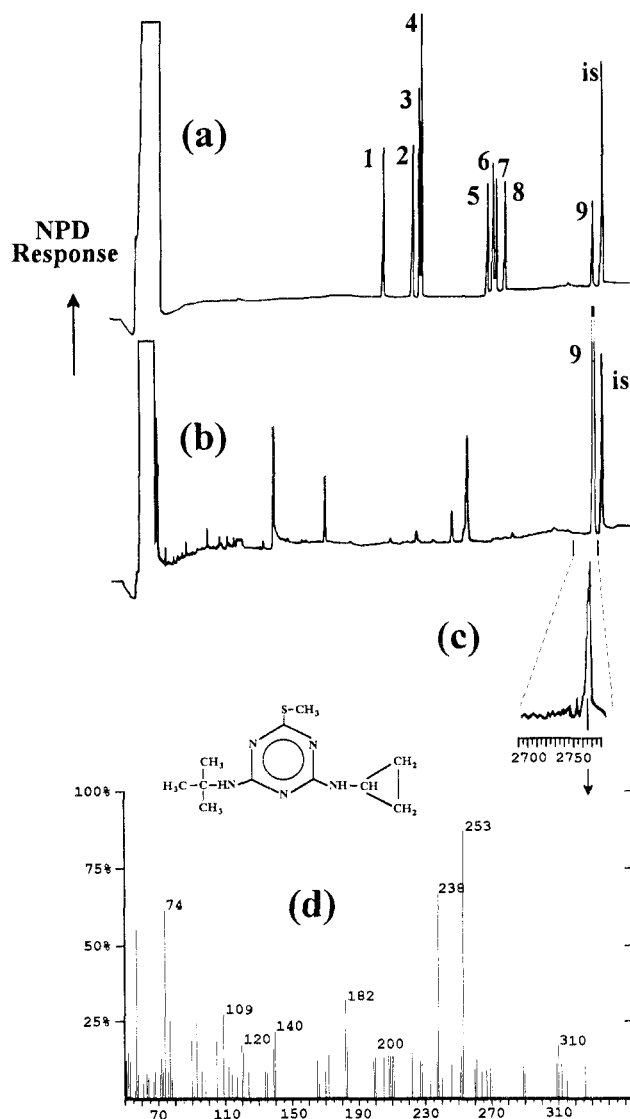


Figure 2. Examples of analyses used to quantify 2-methylthio-4-*tert*-butylamino-6-cyclopropyl-*s*-triazine (IRGAROL 1051) in coastal water samples. (a) Capillary GC–NPD chromatogram of standard herbicides (approximately 0.4 ng of each injected). Peak numbers correspond to (1) prometon, (2) propazine, (3) atrazine, (4) simazine, (5) prometryn, (6) ametryn, (7) simetryn, (8) terbutryn, (9) IRGAROL 1051, and (is) chlorthion, which was selected as the internal standard. GC conditions are described in the text. (b) Capillary GC–NPD chromatogram (run under the conditions specified for panel a) of the extract obtained for the sample from Cap Ferrat marina (sample station no. 12; Figures 1 and 3). The internal standard (chlorthion) was spiked at 50 ng L⁻¹, and the concentration of IRGAROL 1051 was determined to be 430 ng L⁻¹. (c) Relevant portion of a total ion current chromatogram obtained by capillary GC–mass spectrometric analysis (using a Nermag 1010T instrument) of a concentrated coastal water extract. The corresponding mass spectrum obtained for the peak with the same retention time as IRGAROL 1051 is shown in panel (d) with the molecular structure of IRGAROL 1051 inset.

which water was then removed using anhydrous sodium sulfate. After concentration using a gentle stream of nitrogen (to approximately 100 μ L), aliquots (3 μ L) were

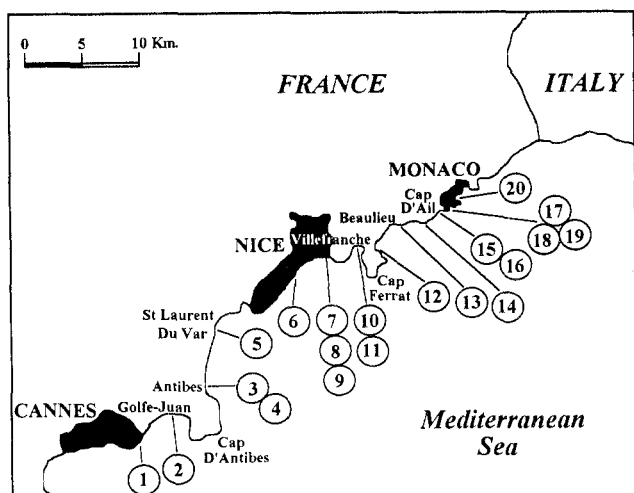


Figure 1. Locations of sampling stations on the Côte d'Azur coastline.

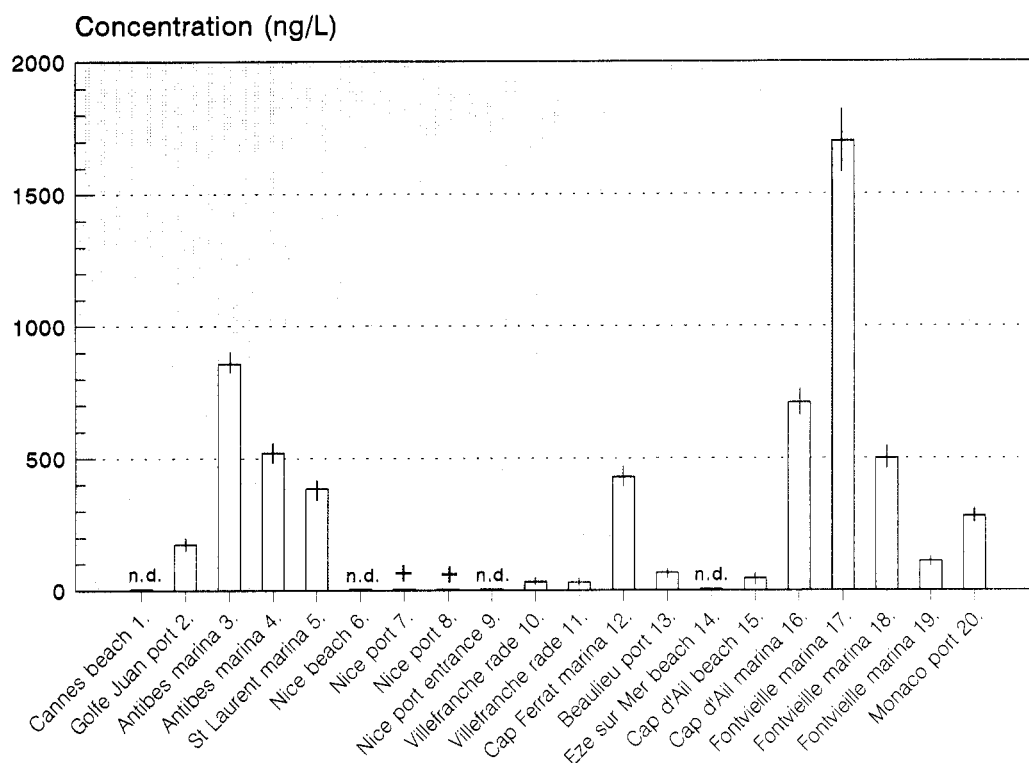


Figure 3. Concentration of 2-methylthio-4-*tert*-butylamino-6-cyclopropylamino-*s*-triazine (IRGAROL 1051) in water samples from the Côte d'Azur coastline. Error bars indicate the analytical variability (as determined from triplicate analyses of a single homogenized sample). Locations of the individual sampling stations correspond to the numbers shown in Figure 1. n.d. indicates not detected (less than 5 ng L⁻¹). + indicates detected but not quantifiable (between 5 and 15 ng L⁻¹).

injected into a capillary gas chromatograph (GC: Hewlett Packard 5890) fitted with a nitrogen-phosphorus detector (NPD). GC conditions were as follows: 25 m × 0.25 mm i.d. OV1701 fused silica capillary column; carrier gas He at 1.2 mL min⁻¹; temperature program: 50 °C for 1 min, 50–170 °C at 40 °C min⁻¹, 170–240 °C at 2 °C min⁻¹, 240–285 °C at 10 °C min⁻¹. The NPD was operated as specified by the manufacturers. To confirm peak identity, samples were analyzed using chromatographic columns of different polarities, and selected extracts were further concentration and were then analyzed by capillary gas chromatography with mass spectrometric detection (electron impact mode). Examples of analyses are shown in Figure 2. Reagent blanks (obtained by analyzing double-distilled water) revealed no contamination from triazine herbicides over the detection limit of the analytical technique (typically <5 ng L⁻¹). Recoveries of IRGAROL 1051 spiked into double-distilled water (at 100 ng L⁻¹) averaged 85% (SD ± 15%; *n* = 3).

Results and Discussion

Concentrations of 2-methylthio-4-*tert*-butylamino-6-cyclopropylamino-*s*-triazine in the Côte d'Azur samples are shown in Figure 3. Measurable levels of the compound were encountered in most samples. Highest concentrations are shown to be associated with yacht marinas which primarily house pleasure craft. Samples from the marinas investigated contained an average concentration of 650 ng L⁻¹ (ranging from 110 to 1700 ng L⁻¹). Ports, which generally have a lower density of pleasure craft and more and larger "working" vessels, are shown to have lower concentrations of the herbicide. In the samples taken from the Côte d'Azur ports, the average concentration was 88 ng L⁻¹ (with levels ranging from <5 to 280 ng L⁻¹). It is

possible that the additive is more frequently used in those paints applied to pleasure craft, although the often sedentary nature of leisure yachts probably exacerbates the situation. Analyses of samples from open beaches at Nice, Cannes, and Eze-sur-Mer revealed negligible contamination, and the low but measurable concentrations associated with waters from Cap d'Ail and Villefranche can be explained by their proximity (<0.5 km) to contaminated harbor entrances.

Although no previous studies report concentrations of IRGAROL 1051, many describe contamination of environmental waters by other *s*-triazine herbicides (3–8). While IRGAROL 1051 is the only triazine herbicide which is used directly in marine systems, others are far more abundantly applied in agriculture and percolate through to estuarine and coastal locations (7, 8). For example, atrazine concentrations of up to 1 µg L⁻¹ have been reported for Greek coastal waters subject to substantial agricultural runoff (7). Highest levels were shown to occur immediately following widespread application of the compound, and seasonally averaged concentrations were approximately 200 ng L⁻¹. Maximum concentrations of atrazine in the Ebro Delta (Spain), the Rhone Delta (France), and the Northern Adriatic Sea have been reported as 60, 390, and 18 ng L⁻¹, respectively (8). From these data it appears that the IRGAROL 1051 concentrations in the Côte d'Azur samples reported herein can exceed levels of other *s*-triazine herbicides in contaminated coastal environments.

To evaluate the environmental impact of the compound in coastal locations, toxicological data is required. Very little information on the compound is, however, available. Current data relate to the "acute" toxicity and have been published by the manufacturers of the product (9). The

minimal inhibition concentrations (MIC) for the alga *Enteromorpha intestinalis* and various diatoms (including species of *Navicula*, *Nitzschia*, *Amphora*, and *Achnanthes*) are reported to be $10 \mu\text{g L}^{-1}$. No information has, however, been found relating to sublethal effects, and the only inferences which can be drawn relate to comparisons with data for other *s*-triazines. Atrazine has been shown to affect photosynthesis in phytoplankton communities at concentrations as low as $1 \mu\text{g L}^{-1}$ (10). Selective stressing of individual species within ecosystems could, in turn, provide the potential for changes in community structures. In addition, some studies have described genotoxicological effects following exposure to triazines (11).

Conclusions

To inhibit the growth of algae on boat hulls, 2-methylthio-4-*tert*-butylamino-6-cyclopropylamino-*s*-triazine (IRGAROL 1051) is incorporated into some marine paints. The reported data demonstrate the extent of contamination of Côte d'Azur coastal waters by leaching of the compound from pleasure craft. Substantial concentrations (of up to 1700 ng L^{-1}) were encountered in samples from yacht marinas, and dispersion of the herbicide into adjacent coastal areas is evidenced. To evaluate toxicological implications of the contamination, further research is required to provide information on the subacute effects of IRGAROL 1051.

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Author Supplied Registry Numbers: Ametryn, 834-12-8; atrazine, 1912-24-9; chlorthion, 500-28-7; 2-methylthio-4-*tert*-butylamino-6-cyclopropylamino-*s*-triazine, 28159-98-0; prometon, 1610-18-0; prometryn, 7287-19-6; propazine, 139-40-2; simazine, 122-34-9; simetryn, 1014-70-6; terbutryn, 886-50-0.

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