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# MONITORING OF NITRATE AND PESTICIDE CONCENTRATION IN WATER SUPPLIES OF THE AGEAN REGION

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## ABSTRACT

The aim of this study is to investigate the ground water quality of the Aegean Region, Izmir Districts concerning pollution with nitrate and pesticides. Pesticides and fertilizers are widely used in this area. After the evaluation of the pesticide consumption data, the 4 most frequently used pesticides (fenitrothion, propargite, endosulfan and trifluralin) were selected as model substances for testing and optimizing the analytical method. The important environmental properties of these pesticides, such as lifetime toxicity and distribution coefficients were also considered in the selection. The analytical method is based on the solid phase extraction and GC analysis for the isolation and determination of pesticides<sup>1</sup>.

During the months of June 1998, 1999 and 2000 water samples from five districts were obtained from the coastal area of the Aegean Sea (regions of Manisa, Menemen, Özdere, Tire and Urla). In total 79 samples were analysed. The ground water was sampled from deep wells (15 to 160 m) that are being used for the local drinking water supply. The results of our study can be summarized as follows: 13 samples out of the 79 samples studied exceeded the European Drinking Water Standard for Nitrate (50mg/L). The Nitrate concentrations were between 1 and 120 mg/L.

Even though there is a high consumption of pesticides in these areas, pesticides were not detected in the samples. Only two samples from the Tire region showed low concentrations of trifluralin. This result can be explained by the mobility of the pesticides in the unsaturated aquifer. While the mobility of nitrate is very high, infiltration of pesticides into the soil does not take place because of adsorption and/or the degradation process in the soil.

The results of our study indicate that the ground-water quality in the investigated areas is starting to become contaminated by nitrate used as fertilizer in agriculture. The high mobility of nitrate leads to the pollution of deep ground water used as drinking water.

## 1. INTRODUCTION

The global population growth was nearly 90 million in 1996. It is anticipated that the rate of increase will peak around the year 2000 and slow thereafter. The overall population of the globe is still likely to double before the middle of the next century. With the growth of the global population a significant increase in the demand of clean water and clean water sources will also rise.

Access to water in adequate quantity and quality is essential for human health and well-being. Although actions during the past have brought considerable progress in many respects of the quality of water, tens of thousand of people still suffer health effects of inadequate water supply and sanitation.

The process of developing drinking water standards is complex. This complexity is primarily due to the need to integrate scientific knowledge with legal requirements and current societal values. The process flows from determining health risks of various contaminants, or risk assessment, to developing regulatory control options, or risk management. The risk assessment process begins by reviewing all possible adverse effects of a particular contaminant and determining which effects are significant via drinking water. An analysis is made of carcinogenic and non-carcinogenic effects of the particular contaminant. Once the health goal is established, the risk management process is used to determine the regulatory approach and the feasible, enforceable level for each contaminant (1,2).

The maximum concentration level (MCL) is the enforceable numeric standard, usually specified in a

specific concentration level, that the U.S.EPA determines to be feasible. Prior to 1979, there were 22 contaminants regulated under the National Interim Primary Drinking Water Regulations. Since 1987 MCL levels for 8 volatile synthetic organic contaminants have been established and most recently 18 new synthetic organic chemicals and 5 inorganic chemicals were specified (2).

In this investigation our goal is to check and monitor the concentration level of nitrate and pesticides in the İzmir region as indicated by the U.S. EPA Regulations. Nitrate concentrations in surface water and especially in ground water have increased in Canada, the United States, Europe and other areas of the World. In many areas nitrate concentration in ground water has reached serious levels exceeding the nominal limits of 10 mg/L as NO<sub>3</sub>-N(nitrate nitrogen) set by the U.S. EPA or 50 mg/L as NO<sub>3</sub> (nitrate) set by WHO, EEC. The recommended nitrate concentration is below 25 mg/L as NO<sub>3</sub> (nitrate). Main sources of nitrate contamination are excessive usage of nitrogen fertilizers in many agricultural areas. With fertilizers also pesticides are used in agriculture throughout in the world. As a consequence, contamination of the environment with pesticides and their breakdown products is of major concern in environmental protection and control (3,4,5). The MCL of pesticide for drinking water is 0.1mg/L. Our paper will describe some of the research currently being conducted to show the importance of nitrate (4) and pesticide monitoring in the İzmir area. This work is done as a part of the EU project 'Development of a simple technology in drinking water treatment for nitrate and pesticide removal'.

### 1.1 Experimental Procedure

Using statistical research for the most frequently used fertilizers and pesticides data for the İzmir area was supplied by the İzmir Agricultural Office. Table 1 shows that fertilizers are widely used in these areas. The table shows the total geographic areas in km<sup>2</sup> of the selected places. It is known that for Menemen, Manisa, Tire, 80% of the total area is used for agriculture where as only 20% of total area in Urla and Özdere is used. Urla and Özdere are coastal areas of İzmir.

Table 1. Fertilizer used in five selected areas in 1997

| Sample Collecting Places | Area in km <sup>2</sup> | Fertilizer in ton/year |
|--------------------------|-------------------------|------------------------|
| Menemen                  | 650                     | 9434                   |
| Manisa                   | 13810                   | 57250                  |
| Urla                     | 728                     | 1268                   |
| Tire                     | 802                     | 2010                   |
| Özdere                   | 55                      | 256                    |

Table 2. Commonly consumed pesticides in Turkey

| Pesticide               | Ton/year (in İzmir) | Ton/year (in Turkey) |
|-------------------------|---------------------|----------------------|
| 2,4 D Esters and amines | 18                  | 2080                 |
| Methylbromide           | 31                  | 780                  |
| Trifluralin             | 90                  | 759                  |
| Copperoxychloride       | Unknown             | 684                  |
| Sulfur                  | Unknown             | 498                  |
| Mancazeb                | Unknown             | 362                  |
| Dichlorvos              | 23                  | 278                  |
| Endosulfan              | 9                   | 278                  |
| Propanyl                | Unknown             | 241                  |
| Propineb                | 27                  | 211                  |
| Carbosulfan             | Unknown             | 149                  |
| Fenitrothion            | Unknown             | 140                  |
| Captan                  | 1                   | 137                  |
| Maneb                   | 11                  | 134                  |

Five of the most common and easily analysed pesticides were selected for the analysis. Our selection was also based on the environmental properties of each pesticide for example the toxicity, lifetime and distribution coefficient of the pesticides.

For the pesticide analysis the water samples were extracted with solid phase extraction methods and samples were measured in the GC-MS-MS system. The solid phase extraction proved to be an effective method for the enrichment and isolation of pesticides from water samples. Compared with other traditional methods such as liquid extraction, solid phased extraction reduces the sample handling and solvent consumption. The most popular for solid phased extraction of pesticides from water is octadecyl-bounded silica. The analytical method to be used in the work is outlined in Figure 1. The sample areas used in this investigation and wells were selected in the agricultural areas of İzmir. Five different agricultural areas, Menemen, Manisa, Urla, Tire and Özdere, were selected, which average 100 km distnce from the center of Izmir as shown in Figure 2.

From these five places, 79 well samples (which are private wells), were obtained. The water of these wells is being used by farmers for their normal drinking and also for watering the farming area. The depths of the wells are changing between 15 to 160 m deep.

During the months of June 1998, 1999, and 2000 water samples from five districts were examined. The initial nitrate and nitrite analysis of well samples collected were measured on site using Nanocolor 300D spectrophotometer, and within 24 hours a Schimatzu IC was performed. The results of the two measurements coincided with each other.

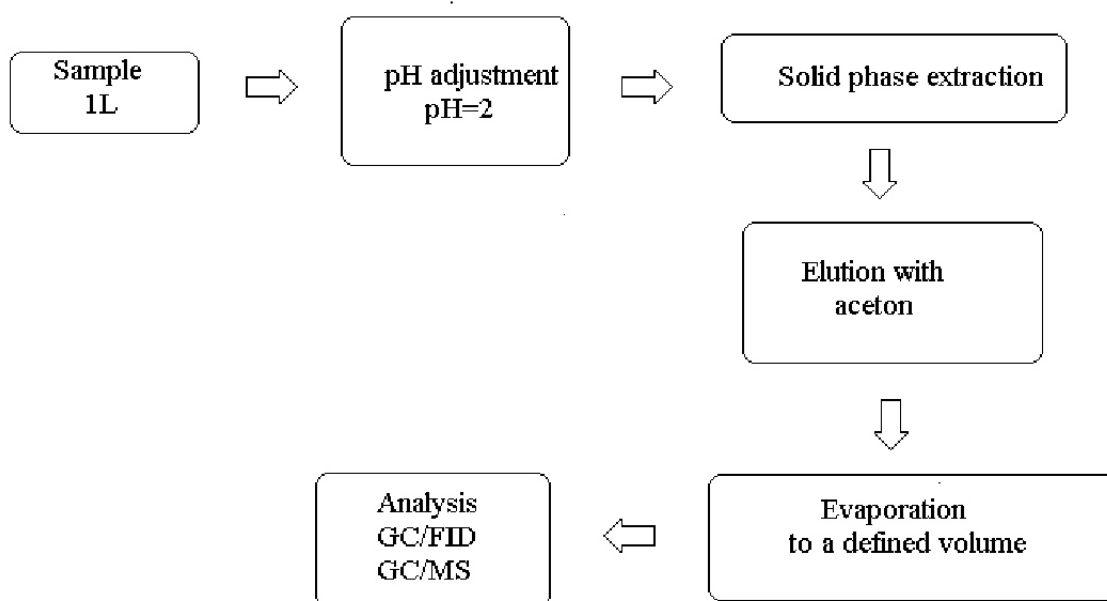


Figure 1: Outline of the method for pesticide analysis.

Table 3. Results of water sample of the İzmir area.

| Sample Places                     | Nitrate in mg/L ( $NO_3^-$ ) | pH  |
|-----------------------------------|------------------------------|-----|
| <b>MENEMEN (14 sample points)</b> |                              |     |
| Ulucak                            | 5                            | 7   |
|                                   | 6                            | 6.9 |
| Günerli                           | 28                           | 6.8 |
| Çavusköy                          | 12                           | 6.7 |
| Asarlık                           | 12                           | 7.3 |
| Emiralem                          | 116                          | 6.2 |
|                                   | 7                            | 6.5 |
| Yahseli                           | 17                           | 6.4 |
|                                   | 53                           | 6.3 |
| <b>MANISA (12 sample points)</b>  |                              |     |
| Muradiye                          | 21                           | 6.8 |
|                                   | 8                            | 6.7 |
|                                   | 5                            | 6.9 |
| Gülbahçe                          | 7                            | 6.8 |
|                                   | 10                           | 6.8 |
| Hacirahman                        | 89                           | 6   |
| Nuriye                            | 14                           | 7.2 |
| Kemiklidere                       | 29                           | 6.8 |
| Lütfiye                           | 19                           | 7.3 |
| <b>URLA (14 sample points)</b>    |                              |     |
| Kuşçular                          | 52                           | 6.5 |
|                                   | 117                          | 7.4 |
|                                   | 120                          | 7.2 |
|                                   | 93                           | 7.5 |
|                                   | 83                           | 7.6 |
|                                   | 70                           | 7.4 |
| <b>TÝRE ( 28 sample points)</b>   |                              |     |
| Çiniyeri                          | 5                            | 6.9 |
| Gökçen                            | 40                           | 6.7 |
| Kahrat                            | 41                           | 6.5 |
| Pınarlı                           | 18                           | 6.8 |
| Akçasehir                         | 51                           | 6.5 |
| Alaylı                            | 45                           | 6.3 |
| Büyükkale                         | 39                           | 7.2 |
| Üzümler                           | 13                           | 6.6 |
| Ayaklıkiri                        | 29                           | 6.6 |
| Mahmutlar                         | 12                           | 6.6 |
| Akkoyunlu                         | 5                            | 6.8 |
| <b>ÖZDERE (11 sample points)</b>  |                              |     |
| Cumhuriyet                        | 54                           | 6.8 |
|                                   | 44                           | 6.9 |
| Orta                              | 63                           | 7.2 |
|                                   | 51                           | 6.6 |

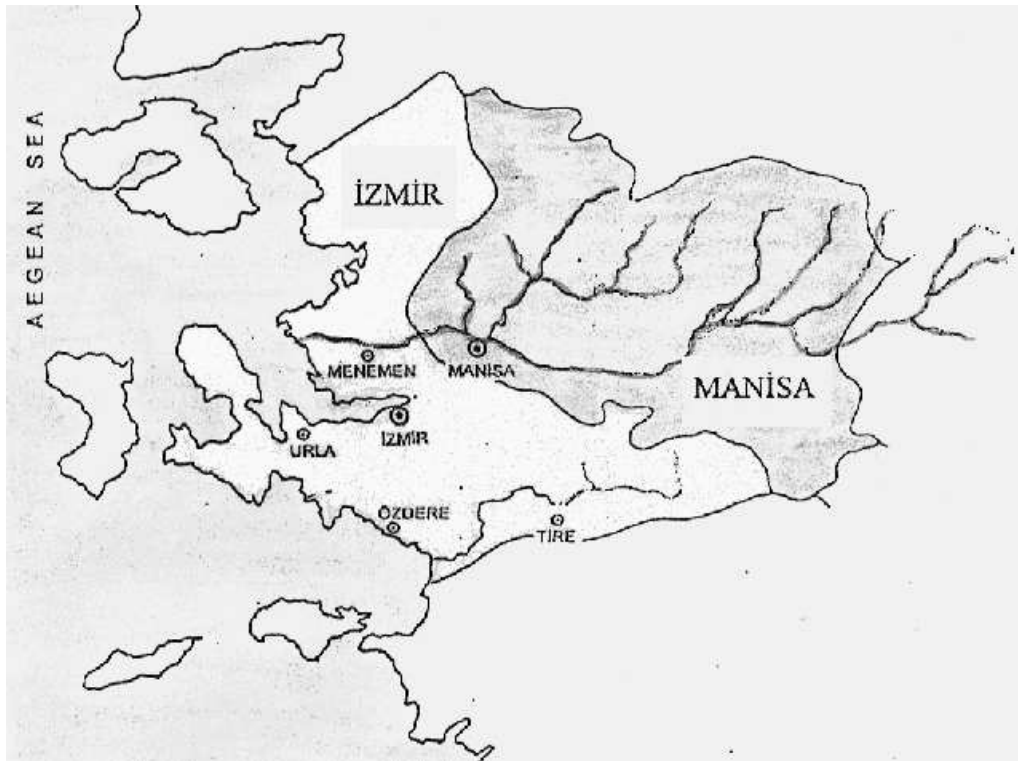


Figure 2. The study area

## 2. RESULTS AND DISCUSSION

The samples were obtained from the five areas and were analyzed. Table 4 shows the areas sampled and the number of sample points along with the village names. Although 79 samples were analyzed only the data where the reading exceeds 5mg/L  $\text{NO}_3^-$  concentration is shown. Forty well sample points show values smaller than 5mg/L nitrate, whereas the remaining samples show readings above 5 mg/L  $\text{NO}_3^-$ . For all the 79 samples the Nitrite values were below 0.05 mg/L  $\text{NO}_2^-$  value. The table also shows that 13 well samples exceed the U.S. EPA and EC and WHO established MCL of 50mg /L for Nitrate. Urla where 14 samples were collected the MCL of 6 wells exceeded the level of 50mg/L, with the other areas only one or two wells exceeded the MCL. It should be noted the wells of the Urla region are only 15-30 m deep whereas the other 4 areas' wells are between 15 and 160m.

Table 4. Nitrate data distribution in five selected area

| Sample Places | Number of sampling points | Number of sampling point >50mg/L |
|---------------|---------------------------|----------------------------------|
| Menemen       | 14                        | 2                                |
| Manisa        | 12                        | 1                                |
| Urla          | 14                        | 6                                |
| Tire          | 28                        | 1                                |
| Özdere        | 11                        | 3                                |

Pesticide was also tested in the samples. Only two samples show a small concentration of trifluralin. The sample point was in the villages of Ayaklıkırı 0.01mg/L and Akkoyunlu 0.023 mg/L of the Tire region. These wells were at the depths 52 m and 22 m respectively. The finding of only two wells with concentration of trifluralin is somewhat of a mystery considering high use of trifluralin (Table 5) for the Izmir region. Additional testing of the 79 wells may need to be carried out using seasonal data. Our samples may have been collected either too early or too late in the agricultural seasons of the 5 areas. Hence only two wells showing trifluralin levels.

Table 5. The selected pesticides consumption in the Izmir area

| Pesticide   | kg/year |
|-------------|---------|
| Endosulfan  | 9420    |
| Fenitrotion | 2148    |
| Propargit   | 10934   |
| Trifluralin | 89813   |

In conclusion monitoring of these areas needs to be carried out on a continuous basis. This monitoring would establish the high and low use seasonally of fertilizers and pesticides in this region. Monitoring and proper instructional use of fertilizers and pesticides used by the farmers of this region should lower the high contamination levels of the regions' water supplies. The end result would be health, welfare and environmental factors for the peoples of these regions.

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<sup>1</sup> Pesticide analysis was carried out at the Engler-Bunte-Institut, University of Karlsruhe, Germany.