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# Nitrate in Drinking Water in the West German Wine-Growing Areas of Baden and Württemberg

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## Nitrate in Drinking Water in the West German Wine-Growing Areas of Baden and Württemberg

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Nitrate is regarded as a substance whose presence in drinking water is not considered as desirable. If reduced to nitrite it may cause methemoglobinemia in infants. Onward reaction with amines capable of coupling will result in the formation of nitrosamines. Excessive use of fertilizers in agriculture is the most frequent cause of elevated nitrate contents of drinking water. To quantify this problem, drinking water was sampled at taps at 200 sites arranged on a grid covering the wine-growing areas of Baden and Württemberg. These samples were examined for their content of nitrate, chloride, and sulphate by means of ion chromatography.

Clearly elevated nitrate contents were revealed by the results of measurements: 13% of samples showed values above the maximal concentration admissible under the EC Drinking Water Directive of  $50 \text{ mg NO}_3^-/1$  and 42% above the EC guide level. The excessive levels were mostly found in the regions of Kaiserstuhl-Tuniberg-Markgräflerland and Württembergisch Unterland. Many samples with an elevated nitrate content exhibited also elevated sulphate contents. The high nitrate levels are attributed to the use of nitrogen fertilizers in the vineyards.

KEY WORDS: Ion chromatography, determination of nitrate, drinking water, West German wine-growing areas, nitrogen fertilizer.

#### INTRODUCTION

Nitrate is considered to be an undesirable substance in drinking water. When considering the toxicity of nitrate and its metabolites, one can distinguish between three ranges<sup>1</sup> (Figure 1): the effect of the nitrate ion

<sup>&</sup>lt;sup>†</sup>Presented at the 12th Annual Symposium on the Analytical Chemistry of Pollutants, Amsterdam, April 82.



FIGURE 1 Physiological activity of nitrate ions.

itself is described as primary toxicity. The FAO/WHO found in animal experiments an acceptable daily intake of around 220 mg for adults.<sup>2</sup> Only when absorbed in greater quantities nitrate causes abdominal pains, diarrhoea and vomiting.<sup>3</sup> Nitrate is however reduced to nitrite (secondary toxicity). The formation of nitrite occurs mainly in the gastro-intestinal tract with the participation of bacteria from the small intestine, powdered milk products or vegetables.<sup>4</sup> Even in small quantities nitrite leads to methemoglobinemia in infants.<sup>5</sup> Under acid conditions nitrite reacts with amines which are able to couple to form nitrosamines (tertiary toxicity). The carcinogenicity of this class of substance has been clearly proved in animal experiments. At present, there is no known species of animal which does not develop tumors when fed with nitrosamines. The carcinogenic effects also occur when nitrite and the corresponding amines are administered.<sup>4</sup>

#### EXPERIMENTAL CONDITIONS

Nitrate in drinking water is mostly considered as being the result of nitrogenous fertilization of specific cultures.<sup>6</sup> In earlier analyses of the nitrate content in drinking water throughout the Federal Republic of Germany, we were able to ascertain the accumulation of excessively high nitrate values in West German wine-producing regions.<sup>7,8</sup> In order to quantify this problem, we took water samples, covering the whole area, from 200 taps for consumers in the wine-producing regions of Baden and Württemberg. The drinking water samples were examined by means of ion chromatography for their anionic parameters: nitrate, chloride, fluoride, phosphate and sulphate. The cations aluminium, lead, borron, beryllium, barium, cadmium, calcium, chromium, iron. copper, manganese, magnesium, nickel, sodium, strontium, silicon and zinc were determined by way of plasma emission spectroscopy. In addition, the cumulative parameters pH value, organically combined carbon, m value and electrical conductivity were measured. The data are stored in a computer and are available for further investigations.

#### FINDINGS

The nitrate contents in drinking water in the wine-producing regions of Baden and Württemberg contrast markedly with those from the whole of the Federal Republic of Germany<sup>7,8</sup> (Figure 2): whereas already 5% of



FIGURE 2 Nitrate contents of drinking water of the Federal Republic of Germany.

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the samples from the whole of the Federal Republic of Germany exceed the admissible maximum concentration of 50 mg/l specified in the EC Directive for Drinking Water,<sup>9</sup> as many as 13% exceed this level in the regions Baden and Württemberg. There are clear differences in the frequency distributions in particular concerning the guide value of 25 mg/l specified in the EC Directive and the lower concentration of 10 mg/l:

FRG altogether:

$$14\% \ge 25 \text{ mg NO}_3^{-}/\text{l}; 34\% \ge 10 \text{ mg NO}_3^{-}/\text{l}$$

Wine-producing regions Baden and Württemberg:

#### $42\% \ge 25 \text{ mg NO}_3^{-}/l; 75\% \ge 10 \text{ mg NO}_3^{-}/l.$

Figure 3 illustrates the regional distribution of the 25 cases where the limit value (13%) was exceeded. This diagram clearly shows that the drinking water in the wine-producing regions of Kaiserstuhl-Tuniberg-Markgräflerland and Württembergisch Unterland is particularly loaded with nitrate. The details of all measured values in both these regions are recorded in Figures 4 and 5. These Figures also illustrate the sumpling places together with their water catchment areas, their nitrate values for drinking water and the areas used in wine production. In the region Kaiserstuhl-Tuniberg-Markgräflerland (Figure 4) the water catchment areas of the sampling places are all situated directly in the vineyards or in their direct vicinity. Therefore, elevated nitrate contents of  $\geq 10 \text{ mg/l}$  were found in nearly all the drinking water samples examined. The water catchment areas of the places, which contain less than 10 mg nitrate/l drinking water, are all situated with one exception (Schallstadt) or near to extremely small wine-producing areas (Feuerbach, in Tannenkirch, Holzen, Grenzach and Herten).

In the region Württembergisch Unterland (Figure 5) the villages around Brackenheim are particularly heavily loaded  $(NO_3^- \ge 50 \text{ mg/l})$ . The corresponding water catchment areas are situated almost exclusively in an extensive wine-producing region. In contrast many of the catchment areas of the localities which are less polluted  $(NO_3^- \le 10 \text{ mg/l})$  are situated in or near to very small wine-producing areas (Oberdingen, Diefenbach, Gündelbach, Spielberg and Benningen).

The samples from the region Württembergisch Unterland also have in part excessively high sulphate contents. Figure 6 shows that almost all samples from this region with more than 50 mg nitrate/l contain sulphate in concentrations which are considerably higher than the median value of all the 200 samples.



● Nitrate in drinking water ≥50 mg/l

FIGURE 3 High nitrate contents of drinking water in the West German wine-growing areas of Baden and Württemberg.



FIGURE 4 Nitrate contents of drinking water of Kaiserstuhl-Tuniberg-Markgräflerland.



FIGURE 5 Nitrate contents of drinking water of Württembergisch Unterland.



FIGURE 6 Correlation between calcium and sulphate in drinking water in Württembergisch Unterland ( $NO_3^- \ge 50 \text{ mg/l}$ ).

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Sulphate is also used as mineral fertilizer in viticulture.<sup>10</sup> In addition, it is pointed out in scientific literature that sulphate can find its way into ground water via artificial fertilizer.<sup>11,12</sup> However, it was not possible to establish a correlation between nitrate and sulphate in the wine-producing region Württembergisch Unterland.

Elevated sulphate contents can also make their way into ground water naturally via the washing out of calcium sulphate deposits.<sup>13</sup> Keller's Hydrologic Atlas<sup>14</sup> too presents the Württembergisch Unterland as an area with locally elevated sulphate contents (>100 mg/l). The sulphate contents in drinking water which we found in this region show a correlation with their calcium values (Figure 7). Therefore, it could be concluded that the excessively high sulphate contents in the corresponding samples are not of anthropogenic origin.



FIGURE 7 Correlation between nitrate and sulphate in drinking water in Württembergisch Unterland.

#### CONCLUSION

By comparing the nitrate contents in drinking water in the whole of the Federal Republic of Germany with those in the wine-producing regions of Baden and Württemberg (Figure 2), it is possible to establish a connection between these high levels and nitrogenous fertilization of the vineyards. Consideration of the regional locations of particularly burdened localities makes this connection even clearer (Figures 4 and 5).

In most European countries the level of nitrate in ground water tends to be on the increase.<sup>3,15</sup> Against the background of infant methemoglobinemia and the possible formation of carcinogenic nitrosamines, efforts must be made to counteract this development. Therefore, the reduction of nitrogenous fertilization to an ecologicallyacceptable level must be discussed.

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