

Nitrosamines – a water safety risk?



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Nitrosamines are probable human carcinogens. As well as being ingested with food, these substances are produced by chemical reactions in the stomach. In the light of findings concerning contamination of drinking water in the US and Canada, we investigated whether nitrosamines could also pose a risk to water resources in Switzerland.

In the mid-1990s, high concentrations of *N*-nitrosodimethylamine (NDMA) were found in chlorinated and chloraminated drinking water in parts of the US and Canada. Subsequent studies revealed that NDMA in drinking water is mainly formed by the reaction of organic nitrogen precursors with chloramine [1] (Fig. 1). These nitrogen precursors derive primarily from wastewater and are not completely degraded at wastewater treatment plants (WWTPs). Common to these compounds is the presence of a dimethylamine group, as occurs in many pharmaceuticals, pesticides (e.g. diuron) and industrial chemicals (e.g. dimethylamine). Chloramine, in contrast, is either added to water directly in the chloramination process or is formed during chlorination from hypochlorite and available ammonium. Increased concentrations of nitrosamines are therefore to be expected in cases where drinking water is – knowingly or unknowingly – abstracted from waterbodies receiving wastewater inputs and disinfected with chlorine or chloramine.

NDMA and other *N*-nitrosamines can enter wastewater from a variety of sources. These compounds are formed from amines in a range of technical processes, e.g. in roasting, in the production of rubber, paints and detergents, in tanneries and when semisynthetic cooling lubricants are used. In Switzerland, these sources are more relevant since drinking water in this country is rarely chlorinated and never chloraminated. Swiss water resources are not generally exposed to significant wastewater inputs, but local releases of contaminated wastewater cannot be ruled out. We therefore wished to find out whether and to what extent wastewater in Switzerland is contaminated with nitrosamines, and whether these substances are effectively eliminated in the course of treatment. For this purpose, we used a high-performance analytical method newly developed by our group, which is also

suitable for determining not previously detectable – non-volatile and thermally unstable – nitrosamines [2].

Nitrosamines in Swiss wastewater. To gain an overview of nitrosamine contamination of wastewater in Switzerland, studies were carried out at 20 WWTPs. Here, 24-hour composite samples were collected on a single occasion at various stages of the treatment process – after primary and secondary treatment and (where applicable) after sand filtration. In addition, in order to document variability over time, 24- to 72-hour composite samples were collected at the WWTP Wüeri in Regensdorf on 16 occasions between 2006 and 2008. In each case, we analysed samples for eight different nitrosamines down to a concentration of 1 ng/l.

Nitrosamines were detected at all 20 WWTPs. The highest concentrations were measured in primary effluent, lying between 1 and 89 ng/l for NDMA (Fig. 2) and between 4 and 31 ng/l for *N*-nitrosomorpholine. NDMA concentrations at the WWTP in Regensdorf varied over time from not detectable to maximum levels close to 1 µg/l (Fig. 3). In contrast, concentrations of nitrosomorpholine (between 3 and 30 ng/l) showed considerably lower variation. Another four of the target nitrosamines occurred less frequently in the wastewater samples, with concentrations up to 25 ng/l. Two of the nitrosamines were not detected at all.

Biological wastewater treatment substantially reduced nitrosamine contamination at most of the WWTPs, with post-treatment concentrations generally lying below 20 ng/l. On average, the elimination rates were 70 % for NDMA, 40 % for *N*-nitrosomorpholine and 70–90 % for the other nitrosamine compounds, although the rates varied (in some cases widely).

Our results indicate that substantial peak concentrations of certain nitrosamines may be attained in wastewater, which are

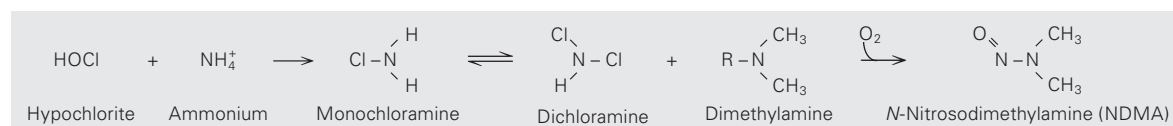


Fig. 1: Formation of *N*-nitrosodimethylamine from dimethylamine and chloramine.

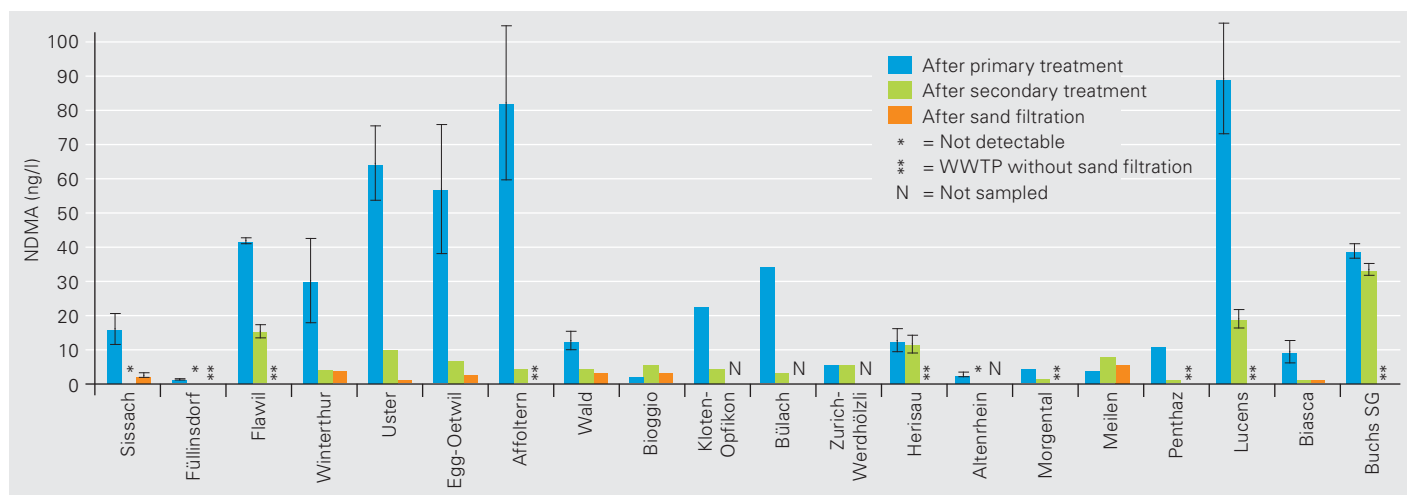


Fig. 2: *N*-Nitrosodimethylamine concentrations in wastewater at various stages of treatment in 20 Swiss plants.

presumably attributable to individual releases from as yet unidentified industrial sources. However, thanks to the generally high treatment efficiency at WWTPs, nitrosamine contamination of treated wastewater is relatively low in Switzerland.

Nitrosamines in water recycling. In contrast to Switzerland, drinking water resources are overexploited in many parts of the

world, and as a result wastewater is increasingly being recycled as drinking or process water. As part of the EU-funded RECLAIM WATER project [3], we studied the occurrence of nitrosamines at the Wulpen/Torreele plant on the Belgian North Sea coast. At this facility, municipal wastewater is treated in a conventional two-stage WWTP and additionally undergoes ultrafiltration and reverse osmosis so as to largely eliminate pathogenic micro-organisms, macro- and micropollutants. The purified wastewater is infiltrated through ponds into an overexploited aquifer in the dune area to prevent seawater intrusion. After a residence time of about 40 days, the groundwater is abstracted for drinking water production (Fig. 4).

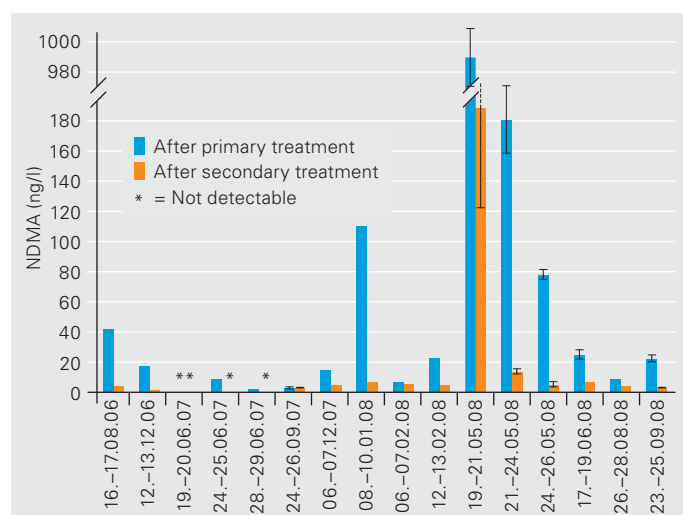
Before and after the two-stage treatment process, only low concentrations of NDMA and *N*-nitrosomorpholine were found in wastewater (less than 10 ng/l).

Nitrosamines derived from food and produced in the body

Since the 1970s, nitrosamines have been known to occur in foodstuffs in concentrations of up to several micrograms per kilogram – in smoked and nitrite-cured meat and fish, and in malt products such as beer. Nitrosamines have also been and continue to be found in a variety of other consumer goods, such as rubber products (e.g. dummies) and cosmetics, as well as in tobacco smoke. Even though, as a result of modified production processes, foodstuffs now contain significantly lower levels of nitrosamines, recent estimates assume that the dietary intake for adults is about 80–300 ng per day [4].

In addition, endogenous nitrosamine formation contributes to total exposure: in the stomach, nitrate is reduced to nitrite, which under acidic conditions reacts with food-borne amines to form nitrosamines. Estimates in the literature vary widely, ranging from 100 ng to as much as 20 µg per day. Endogenous nitrosamine formation is thus probably responsible for the largest portion of the total load, but is strongly dependent on dietary habits [4].

Fig. 3: Variation in concentrations of *N*-nitrosodimethylamine at the Regensdorf wastewater treatment plant.



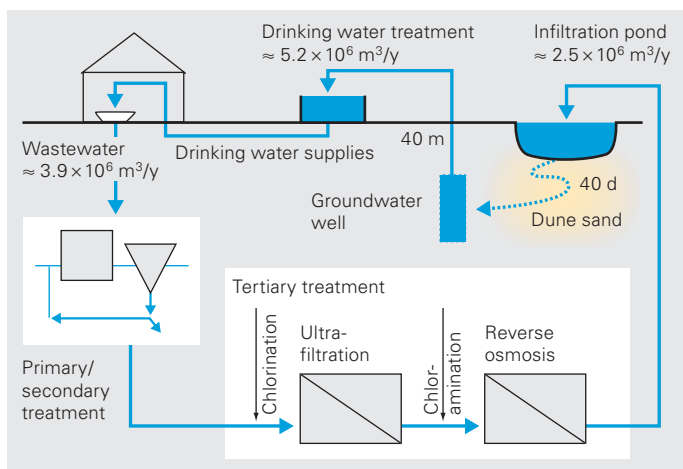


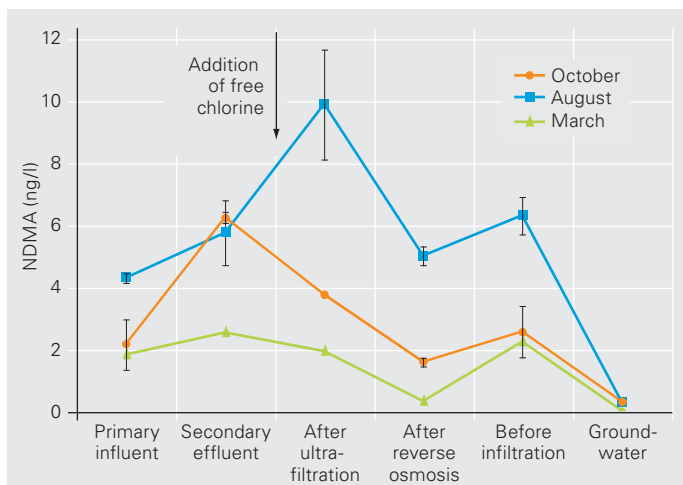
Fig. 4: Flow diagram of wastewater treatment, artificial groundwater recharge and drinking water production at the Wulpen/Torreele plant in Belgium.

When higher doses of chlorine or chloramine are used – as is the case in the summer – to prevent fouling of the ultrafiltration and reverse osmosis membranes, NDMA is formed (Fig. 5). In contrast to most inorganic ions and organic micropollutants, only about 50 % of this substance is removed by reverse osmosis, as the small, uncharged and highly polar NDMA molecules can pass through such membranes. NDMA is however degraded in groundwater, and it was therefore not detected either in groundwater or in the treated drinking water. The low concentrations of *N*-nitrosomorpholine are reduced to below the detection limit by reverse osmosis.

Our studies furthermore demonstrate that nitrosamine precursors are retained by reverse osmosis with an efficiency of more than 98 %. Accordingly, the formation of nitrosamines is very unlikely even if drinking water is chlorinated.

Fig. 5: Concentrations of *N*-nitrosodimethylamine measured on three sampling occasions at the Wulpen/Torreele plant.

Free chlorine added: March and October 1.5 mg/l, August 2.75 mg/l.



Nitrosamine limits

Nitrosamines are carcinogens or, more precisely, procarcinogens, which have to be activated in the body before they can exert any harmful effects. For substances of this kind, it is not possible to define specific limits on the basis of classical dose-response relationships. Limits are therefore based on the tolerable excess risk of developing cancer, which is extrapolated from animal experiments. For *N*-nitrosodimethylamine (NDMA), the US Department of Health and Human Services in 2005 determined the 1-in-a-million cancer risk level with lifetime consumption of drinking water to be 0.7 ng/l; for other nitrosamines the values lie in the range 0.2–16 ng/l.

In Switzerland, nitrosamine levels in drinking water have not been regulated to date, while in the Netherlands, Germany and some US states, (provisional) guideline or action levels of 10 ng/l have been proposed or specified for NDMA.

Nitrosamines to be avoided as far as possible! Our results indicate that, unlike in the US and Canada, drinking water supplies in Switzerland are unlikely to be contaminated with nitrosamines. Far greater quantities are ingested with our food or produced by our own body (see Box on p. 26). Compared with the overall daily intake, which for an adult may lie in the microgram range, the guideline values of approx. 10 ng/l proposed for drinking water (see Box on p. 27) appear to be very low. Nonetheless, any additional intake of carcinogenic substances in drinking water is to be avoided – especially for infants and children, whose ingestion of nitrosamines with food is certainly much lower. ○ ○ ○

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