ANION EXCHANGE RESINS AS SOURCES OF NITROSAMINES AND NITROSAMINE PRECURSORS

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Abstract

RILEY C FLOWERS: Anion Exchange Resins as Sources of Nitrosamines and Nitrosamine Precursors
(Under the direction of Philip C. Singer)

Nitrosamines are a family of potent chemical carcinogens including, among others, N-nitrosodimethylamine (NDMA), N-nitrosodiethylamine (NDEA), N-nitrosodi-n-propylamine (NDPA) and N-nitrosodi-n-butylamine (NDBA). NDMA and other nitrosamines have been identified as disinfection byproducts. They are regulated in the State of California and are candidates for Federal regulation.

Anion exchange resins, used for the removal of anionic contaminants from drinking water, consist of polymer networks with positively charged amine groups. Resins are often synthesized using trimethylamine (TMA), triethylamine (TEA), tri-n-propylamine (TPA) or tri-n-butylamine (TBA) which can react with chloramines to form NDMA, NDEA, NDPA and NDBA, respectively. Drinking water treatment plants using anion exchange resins have been found to have higher levels of NDMA in finished waters.

The objective of this research was to investigate the potential relationship between the use of anion exchange resins in drinking water treatment and the presence of nitrosamines and nitrosamine precursors in finished waters. A wide array of resins, representing those commonly used in practice, was investigated through bench-scale

batch contact experiments, bench-scale continuous-flow column experiments, and measurements at water utilities using anion exchange for treatment.

In the batch experiments, resins were found to release nitrosamines and their precursors after one hour of contact. Resins manufactured with TEA or TBA were found to release NDMA precursors in addition to NDEA or NDBA precursors. In column experiments, resins released high nitrosamines and precursors in the first 10 bed volumes of flow. Regeneration with NaCl resulted in a spike in precursor release, as did flow interruptions. The introduction of chlorine or preformed monochloramine resulted in increases in nitrosamines. Explanations for the presence of precursors and their increased release during regeneration and flow interruption are offered, and a mechanism for nitrosamine formation via reactions with free chlorine and monochloramine is proposed.

A study of ten full-scale treatment plants using anion exchange resins found that three contained nitrosamines and five contained precursors in their anion exchange effluents. Experiments suggested that resins can be washed clean of any residual nitrosamines and precursors, and field observations confirmed that resins that have been in place for longer periods of time release lower levels of precursors.

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Chapter 1. Introduction

Background

Nitrosamines

Nitrosamines are a family of highly potent chemical carcinogens including, among others, N-nitrosodimethylamine (NDMA), N-nitrosodiethylamine (NDEA), N-nitrosodi-n-propylamine (NDPA) and N-nitrosodi-n-butylamine (NDBA) (see Table 1.1). In recent years, nitrosamines have been identified as emerging nitrogenous disinfection byproducts (N-DBPs) and have been the subject of extensive research in the field of water quality.

Table 1.1. Nitrosamines.

Name	Abbreviation	Chemical Structure
N-nitrosodimethylamine	NDMA	$(CH_3)_2N\text{-}N{=}O$
N-nitrosodiethylamine	NDEA	$(CH_3CH_2)_2N\text{-}N{=}O$
N-nitrosodi-n-propylamine	NDPA	$(CH_3CH_2CH_2)_2N\text{-}N{=}O$
N-nitrosodi-n-butylamine	NDBA	$(CH_3CH_2CH_2CH_2)_2N\text{-}N{=}O$

The United States Environmental Protection Agency (USEPA) Integrated Risk Information System (IRIS) lists drinking water concentrations corresponding to a 10^{-6} lifetime cancer risk at 0.7 ng/L for NDMA, 0.2 ng/L for NDEA, 5 ng/L for NDPA, and 6 ng/L for NDBA (USEPA, 2011a). For the most harmful of the trihalomethanes, bromodichloromethane, IRIS lists a concentration of 600 ng/L for the same risk level.

Hence, nitrosamines are orders of magnitude more carcinogenic than the regulated trihalomethanes.

Nitrosamines have been the subject of drinking water regulation by different agencies. The Ontario Ministry of the Environment has set an Interim Maximum Allowable Concentration of 9 ng/L for NDMA in drinking water (Ontario Ministry of the Environment, 1998). The California Department of Public Health has set a Notification Level (the level at which a governing body must be notified and consumer notification is recommended) of 10 ng/L for NDMA, NDEA and NDPA in drinking water, with Response Levels (levels at which a water source may be removed from service) at 100, 300 and 500 ng/L, respectively (CA DPH, 2009), and the Massachusetts Department of Environmental Protection has set an Office of Research and Standards Guideline of 10 ng/L for NDMA in drinking water (MassDEP 2004). While the USEPA has not yet set a Maximum Contaminant Level for any nitrosamine, NDMA, NDEA and NDPA are included on Contaminant Candidate List 3 (USEPA, 2011b), and NDMA, NDEA, NDPA and NDBA are being monitored as part of the Unregulated Contaminant Monitoring Rule 2 (UCMR 2) (USEPA, 2011c). Currently, the USEPA is considering regulation of nitrosamines as a group as part of Goal 1 of its new Drinking Water Strategy (USEPA, 2010).

Nitrosamine occurrence in drinking waters

A survey of 21 US and Canadian drinking water treatment plants (Valentine et al., 2006) detected NDMA in the finished water of 18 plants. In all but two cases, NDMA concentrations were below 10 ng/L, a level of regulatory concern in the US. NDMA concentrations were higher in samples collected from distribution systems. A survey of

179 drinking water treatment plants in Ontario (Charrois et al., 2007) found NDMA in 30% of the drinking water systems investigated. The median plant effluent NDMA concentration was < 1.3 ng/L, but the highest effluent concentration detected was 65 ng/L. As in the survey by Valentine et al., (2006), concentrations were generally higher in distribution systems. Both of these studies noted that the use of anion exchange resins or cationic polymers seemed to be associated with higher levels of NDMA. In a study of 6 Japanese treatment plants (Asami et al., 2009), two of the plants had NDMA concentrations above 10 ng/L in samples taken after ozonation. Biologically activated carbon effectively removed NDMA, and only one of the 6 treatment plant effluents had NDMA levels above 3 ng/L. A recent Spanish study (Jurado-Sanchez et al., 2010) found NDMA in 3 out of 16 tap water samples, with a maximum concentration of 10.3 ng/L. NDEA was detected in 2 of the samples, with a maximum concentration of 6 ng/L. A survey of Chinese drinking water treatment plants (Wang et al., 2011) detected NDMA in 7 of 12 finished waters, with a range of 4.6 – 20.5 ng/L. NDEA was also detected in 9 of 12 finished waters, with a concentration range of 1.9 – 16.3 ng/L, and NDBA was detected in 6 of 12 finished waters, with a range of 0.4 – 3.4 ng/L. NDPA was not detected. An analysis of UCMR 2 data (Russell et al., in press) showed that, out of 1,196 drinking water systems sampled, 316 or 24.6% contained NDMA at 2 ng/L or above in the distribution system, with a median NDMA concentration among those plants of less than 10 ng/L. Other nitrosamines were detected much less frequently. NDEA was detected at 3 ng/L or above in 2.2% of the systems and NDB was detected at 4 ng/L or above in 0.4% of the systems. NDPA was not detected in any of the systems sampled.

Mechanism of nitrosamine formation

A mechanism of NDMA formation involving the chlorination or chloramination and subsequent oxidation of dimethylamine (DMA) to form unsymmetrical dimethylhydrazine (UDMH), which can be oxidized to form NDMA, was proposed in different mechanistic studies (Mitch and Sedlak, 2002; Choi and Valentine, 2002a; Choi and Valentine, 2002b). These studies demonstrated that NDMA formation occurs when water is chloraminated or chlorinated in the presence of ammonia, that increasing chloramine doses lead to increased NDMA formation, that chloramine is a source of nitrogen atoms in NDMA, and that DMA is an important NDMA precursor. However, noting that UDMH does not form NDMA at the yield expected based on NDMA yields from DMA and that the UDMH models are not robust over a wide pH range, Schreiber and Mitch (2006) demonstrated that NDMA formation actually depends on dichloramine concentration and, accordingly, proposed a new mechanism. The mechanism is based on the reaction of dichloramine with DMA to form chlorinated UDMH, which is subsequently oxidized by dissolved oxygen to form NDMA (see Figure 1.1). Sufficient dichloramine exists, in disproportionation equilibrium with monochloramine, to account for the formation of NDMA when monochloramine is added to water. This is the currently accepted mechanism of NDMA formation (Nawrocki and Andrzejewski, 2011).

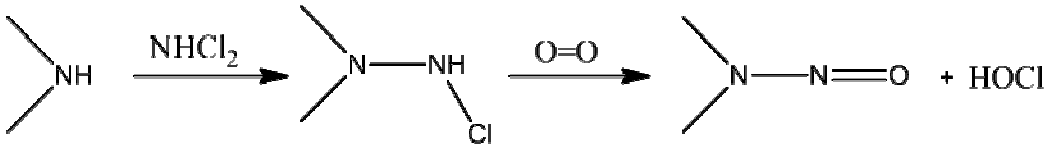


Figure 1.1. Mechanism of NDMA formation from dichloramine and dimethylamine (Schreiber and Mitch, 2006).

Nitrosamine precursors

While DMA has been used as a model NDMA precursor for kinetic and mechanistic investigations, it was noted (Mitch et al., 2003; Chen and Valentine, 2007; Padhye et al., 2009) that DMA levels in natural waters could not account for the amounts of NDMA formed when those waters were chloraminated. Chloramination of natural organic matter (NOM) has been shown to produce significant amounts of NDMA (Gerecke and Sedlak, 2003; Chen and Valentine, 2006; Chen and Valentine, 2007). Dissolved organic nitrogen (DON), a measure of the amount of undefined nitrogen-containing species in NOM, is believed to be an important factor in the formation of NDMA in raw drinking water sources (Lee et al., 2007). It has been shown (Mitch and Sedlak, 2004) that tertiary amines with dimethylamine functional groups can serve as important NDMA precursors and that trialkylamines can degrade to dialkylamines when oxidants/disinfectants are added, which then react to form nitrosamines (Mitch and Schreiber, 2008). Dimethylamine groups within NOM macromolecules are thought to account for the formation of NDMA by NOM. It is likely that diethylamine (DEA), di-n-propylamine (DPA) and di-n-butylamine (DBA), and larger molecules containing these functional groups, serve as analogous precursors to NDEA, NDPA and NDBA, respectively. A recent study by Wang et al. (2011) showed that DEA and DBA in the influent and effluent of drinking water treatment plants were precursors of NDEA and NDBA.

Other chemicals containing DMA functional groups have been shown to form NDMA upon chloramination, including herbicides (Chen and Young, 2008) and pharmaceuticals and personal care products (Kemper et al., 2010; Shen and Andrews,

2011), which may be present in drinking waters with sources impacted by agricultural activity or wastewater discharge. Le Roux et al. (2011) found that 5-(dimethylaminomethyl)furfuryl alcohol, a component of the drug ranitidine, when chlorinated, formed NDMA at a much higher molar yield than that of DMA (74.9% vs 1.2%). This was attributed to the proximity of an electron-dense furan group to the reactive DMA group, which enhances the electrophilic attack of chloramine.

In the context of drinking water treatment, cationic coagulant polymers and anion exchange resins have been identified as sources of nitrosamine precursors. Treatment with polydiallyldimethylammonium chloride (polyDADMAC) was shown to result in increased NDMA formation (Wilczak et al., 2003), and reaction mechanisms for the degradation of polyDADMAC and polyamines to release DMA and form NDMA during chloramination have been proposed (Park et al., 2009). Polyamine undergoes an electrophilic attack by chloramines at the tertiary amine chain ends, proceeding through an imine intermediate, which yields DMA through hydrolysis. PolyDADMAC contains quaternary amine groups throughout the polymer structure. These groups undergo a Hofmann elimination, leading to a tertiary amine that degrades in the same manner as the polyamine chain ends. The relationship between nitrosamines and anion exchange treatment is discussed below.

Anion Exchange

Anion exchange resins are commonly used for the removal of anionic contaminants, such as nitrate, perchlorate, arsenic, chromate, and dissolved organic matter, during drinking water treatment. These resins consist of crosslinked polymer networks (styrene-divinylbenzene or polyacrylate) functionalized with amine groups to

provide positively charged exchange sites. Resins remove anionic contaminants when the negatively charged contaminants are attracted to the positively charged exchange sites. The resins bind contaminants and release harmless chloride ions according to Equation 1.1:

$$\underline{Cl^-} + X^-_{(aq)} \leftrightarrow \underline{X^-} + Cl^-_{(aq)} \quad (1.1)$$

where underlining indicates the resin phase and X^- is an anionic contaminant. Resins are designed to preferentially remove different anions, binding anions for which they have a greater selectivity and releasing less selectively bound anions. A qualitative selectivity spectrum for a typical resin is shown in Equation 1.2, with more selectively bound anions on the left and less selectively bound anions on the right (Dow Chemical Company, 2011a).

$$SO_4^{2-} > NO_3^- > Br^- > CN^- > BrO_3^- > NO_2^- > Cl^- > HCO_3^- > F^- \quad (1.2)$$

As treatment progresses, high-selectivity anions are taken up and fewer exchange sites are available, so that the resin becomes exhausted. To regenerate the resin, the resin is treated with concentrated NaCl and the equilibrium in Equation 1.1 is pushed to the left. The exchange sites release the contaminants into a waste regenerant stream and the resin is again ready for treatment. Resins are typically regenerated at regular intervals over their treatment lifetimes. As resins absorb water differently based on the ionic form that they are in, regeneration causes a change in swelling and places osmotic stress on the resins (Montgomery Watson Harza, Inc., 2005).

Perchlorate (ClO_4^-) contamination poses a unique challenge for anion exchange treatment. Other anions, such as nitrate (NO_3^-) and sulfate (SO_4^{2-}), often occur at much higher concentrations than ClO_4^-, and compete with ClO_4^- for exchange sites (Calgon

Carbon Corporation, 2005). To address this problem, specific anion exchange resins have been developed to selectively bind the large, poorly hydrated ClO_4^- molecule (Gu et al., 1999). These resins have such high selectivities for ClO_4^- that regeneration with Cl^- is impractical and so they are utilized as single-use, non-regenerable resins.

The polymer matrices of resins affect their performance. Acrylic resins are more elastic than polystyrene resins and can handle a greater amount of osmotic stress. Polystyrene resins, on the other hand, are more rigid and are better for high-pressure applications as they resist compression.

An important physical characteristic of resins is pore structure. Resins with macroporous pore structures have highly crosslinked polymer matrices and uniform areas of high charge density, while gel resins take on a looser, amorphous structure. As a result, macroporous resins tend to be more physically stable and to have greater affinities for given anions, while gel resins tend to exhibit much faster exchange kinetics and to have high exchange capacities by weight (Harland, 1994).

Anion exchange resins are classified according to their functional groups. Resins with secondary or tertiary amines at their exchange sites are protonated, and thus positively charged under a limited pH range. Such resins are known as weak base anion exchange resins. Resins with quaternary amines are positively charged at all pH levels and are known as strong base anion exchange resins. Strong base anion exchange resins are further classified into two groups: resins that have trialkylamine groups such as TMA, triethylamine (TEA), tri-n-propylamine (TPA) or tri-n-butylamine (TBA) are known as Type I resins, while resins with dimethylethanolamine (DMEA) functional groups are known as Type II resins.

Different resin functional groups can be used to achieve different selectivities. While resins with TMA functional groups are the simplest, resins with TEA or TBA functional groups are often used for NO_3^- and ClO_4^- removal because the larger alkyl chains effectively block the uptake of SO_4^{2-} (DeSilva, 2003). TBA resins are preferable for some applications because of their greater SO_4^{2-} blocking properties, while TEA resins are preferable in others because the large chains on TBA resins can cause losses in exchange capacity due to the kinetic effects of steric hindrance (Gu et al., 1999). Type II resins are similar to TMA resins, with higher operating capacities and exchange efficiencies but lower chemical stability (Dow Chemical Company, 2011b).

In the case of polystyrene resins, the process of attaching the positively charged functional group to the polymer begins with chloromethylation of the polymer rings, resulting in poly(4-chloromethylstyrene). Trialkylamines or DMEA are then introduced and replace the chlorine groups via nucleophilic substitution, resulting in a positively charged quaternary amine functional group (Kunin, 1963) (see Figure 1.2).

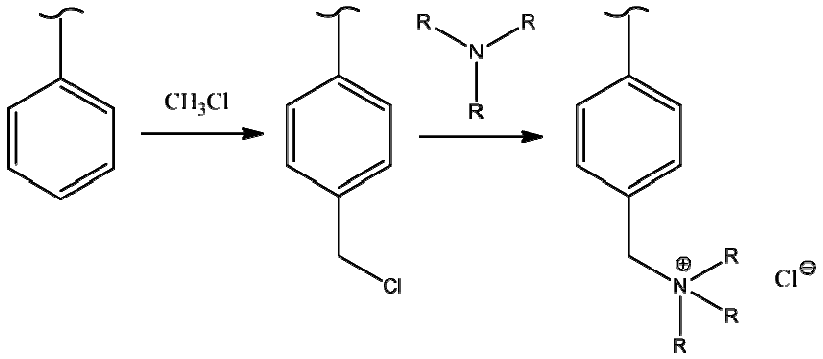


Figure 1.2. Addition of quaternary amine group to polystyrene resin.

Polyacrylic resins are functionalized through the addition of dimethylaminopropylamine (DMAPA). Treatment with methyl chloride produces a positively charged quaternary amine functional group (Harland, 1994) (see Figure 1.3).

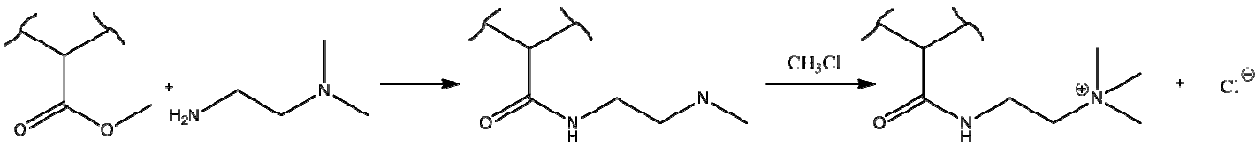


Figure 1.3. Addition of quaternary amine group to polyacrylic resin.

The presence of trialkylamines in the chemical structures of anionic exchange resins and as raw materials for resin synthesis strongly suggests a relationship between anion exchange resins and the potential formation of nitrosamines.

Anion Exchange Treatment and Nitrosamine Occurrence

The link between anion exchange and nitrosamines has been known for some time. Early studies (Fiddler et al., 1977; Gough et al., 1977) reported low µg/L levels of NDMA in deionized water produced by an anion exchange system using Type I TMA resins. NDEA was present when a TEA resin was used. Another study (Kimoto et al., 1980) found that TMA resin produced NDMA in laboratory-scale column contact experiments. The addition of free chlorine in the column feed water led to an increase in NDMA in the column effluent.

More recent studies focusing on nitrosamines as drinking water contaminants found that anion exchange resins used in drinking water treatment released nitrosamines. In what its authors described as a "limited study," four resins, containing DMEA, TMA, TEA and TPA functional groups, were soaked in NaCl and rinsed with deionized water

before being contacted with untreated groundwater, distilled water, and distilled water containing nitrite for 3 hours (Najm and Trussel, 2001). The DMEA and TMA resins released appreciable levels of NDMA (up to 140 ng/L). In this preliminary investigation, the releases of NDEA or NDPA by the TEA and TPA resins were not measured, nor were the releases of nitrosamine precursors. In another study (Kemper et al., 2010), a TMA, a TBA and a DMEA resin were found to release NDMA in continuous-flow column experiments (empty bed contact time of 6 minutes) with a model water buffered at pH 8.5 and containing chloride, sulfate and nitrate. The resins were not cleaned in any way prior to the experiments. The resins released high levels of NDMA precursors (1000 - 11,000 ng/L) at the beginning of the flow experiments but the levels quickly subsided. NDMA precursor levels rose after the resins were regenerated with NaCl, and nitrosamine levels increased considerably when free chlorine or preformed monochloramine was introduced to the feed water. The TBA resin released comparable levels of NDMA and NDBA.

Treatment by anion exchange has been previously identified as a contributory factor for the presence of nitrosamines in finished drinking waters. A study of 21 drinking water treatment plants (Valentine et al., 2006) found that a plant using anion exchange and chlorination had the highest NDMA levels (10-30 ng/L) in the finished water. The study included one other plant employing anion exchange to treat a portion of its water, but the finished water of this plant did not contain similarly high NDMA levels. A survey conducted by the California Department of Health Services (CDHS, 2002) investigated 4 plants using anion exchange. One of the 4 plants had NDMA concentrations (30-34 ng/L) above the California notification level (10 ng/L) for finished waters.

Objectives

As described above, preliminary studies have demonstrated a link between anion exchange resins and nitrosamines, but these studies were limited in scope. Each dealt with only three or four resins out of the wide array of resins used for drinking water treatment applications. Furthermore, these studies focused on NDMA and briefly addressed NDBA, but there are two other carcinogenic nitrosamines that may be associated with the use of anion exchange resins.

Accordingly, the overall objective of this research was to investigate the potential relationship between the use of anion exchange resins in drinking water treatment and the presence of nitrosamines and nitrosamine precursors in finished drinking water. A large number of resins were investigated, representing the array of anion exchange resins used in drinking water treatment practice. The overall objective was pursued as three specific research objectives:

i) to evaluate the release of nitrosamines and nitrosamine precursors by anion exchange resins, specifically addressing the release of multiple nitrosamines and their corresponding precursors by single resins;

ii) to evaluate the effects of different treatment operations on the release of nitrosamines and nitrosamine precursors by anion exchange resins, specifically addressing the release of resins at the beginning of operation and the effects of regeneration, flow interruption, and the presence of free chlorine or monochloramine in column feed water; and

iii) to evaluate the release of nitrosamines and nitrosamine precursors in water treatment practice through sampling of full-scale drinking water treatment plants employing resins previously determined through laboratory experiments to release notable levels of nitrosamines and nitrosamine precursors.

To meet these objectives, controlled bench-scale batch and continuous-flow column studies were conducted, and samples were collected from a number of full-scale treatment plants using anion exchange. Each of these components of the study is presented as a separate chapter in this dissertation:

Anion exchange resins as a source of nitrosamines and nitrosamine precursors. I. Batch Contact Experiments. This chapter summarizes the results obtained from batch contact experiments performed with a large array of resins to assess the release of NDMA, NDEA, NDPA and NDBA and their precursors from resins with different chemical structures and functionalities. Resins releasing high levels of nitrosamines and precursors, or resins releasing more than one nitrosamine with its corresponding precursors were identified for further study. Resin cleaning arose as an important issue, and continuous-flow column experiments were suggested to evaluate nitrosamine and precursor release during rinsing and during subsequent column operations.

Anion exchange resins as a source of nitrosamines and nitrosamine precursors. II. Simulated Treatment Operations. This chapter summarizes the results obtained from continuous-flow column contact experiments conducted with resins of interest as identified during the batch contact studies. Nitrosamine and precursor levels were monitored during column flow to determine the impact of rinsing on nitrosamine and

precursor release. Simulated regenerations and flow interruptions were performed on the resins and increases in nitrosamine and nitrosamine precursor release due to these operations were observed. The results of these experiments suggested that full-scale treatment plant sampling be conducted with attention given to resin regeneration, resin age (time of operation since installation), and downtime.

The impact of anion exchange treatment on nitrosamine and nitrosamine precursor concentrations in full-scale drinking water treatment plants. Samples of anion exchange process influent and effluent were collected at ten full-scale drinking water treatment plants using resins that were studied in previous laboratory investigations. When possible, samples were collected before and after resins were regenerated, or after seasonal downtime. For non-regenerable resins, samples were taken from systems with different resin ages (time in operation). Plants using multiple resins were sampled, and multiple plants using the same resin were sampled. Full-scale field observations were compared to previous laboratory observations to gain insight into nitrosamine and nitrosamine precursor release in drinking water treatment practice.

The major conclusions of the research and recommendations for further study are summarized in Chapter 5.

Chapter 2. Anion Exchange Resins as Sources of Nitrosamines and Nitrosamine Precursors. I. Batch Contact Experiments

Introduction

Nitrosamines are a class of highly potent chemical carcinogens that include, among others, N-nitrosodimethylamine (NDMA), N-nitrosodiethylamine (NDEA), N-nitrosodi-n-propylamine (NDPA) and N-nitrosodi-n-butylamine (NDBA). Nitrosamines, especially NDMA, have been detected in a number of drinking waters (Valentine et al., 2006; Charrois et al., 2007; Zhao et al., 2006; Asami et al., 2009) and are candidates for USEPA regulation (USEPA, 2011b).

The most thoroughly studied nitrosamine, NDMA, has been identified as a byproduct of the disinfection of water with chloramines (Choi and Valentine, 2002a). Extensive research into the mechanism of NDMA formation has shown a two-step process involving dichloramine and dissolved oxygen reacting with dimethylamine (DMA) (Choi and Valentine 2002b; Mitch and Sedlak 2002; Schreiber and Mitch 2005; Schreiber and Mitch 2006). Further study has identified DMA and tertiary amines containing DMA groups as major nitrosamine precursors (Lee et al., 2007).

Anion exchange resins are commonly used for the removal of anionic contaminants, such as nitrate, perchlorate, arsenic, chromate, and dissolved organic matter, during drinking water treatment. Resins are typically composed of a crosslinked polymer (polystyrene-divinylbenzene or polyacrylic) matrix that is functionalized with quaternary amine groups to provide positively charged exchange sites. Resins are

classified according to functional group. Type I resins have trialkylamines – trimethylamine (TMA), triethylamine (TEA), triproplyamine (TPA) or tributylamine (TBA) – at the charged sites, while Type II resins use dimethylethanolamine (DMEA).

In the case of polystyrene resins, the process of attaching the positively charged functional group to the polymer begins with the chloromethylation of the polymer rings, resulting in poly(4-chloromethylstyrene). Trialkylamines or DMEA are then introduced and replace the chlorine groups via nucleophilic substitution, resulting in a positively charged quaternary amine functional group (Figure 2.1) (Kunin, 1963).

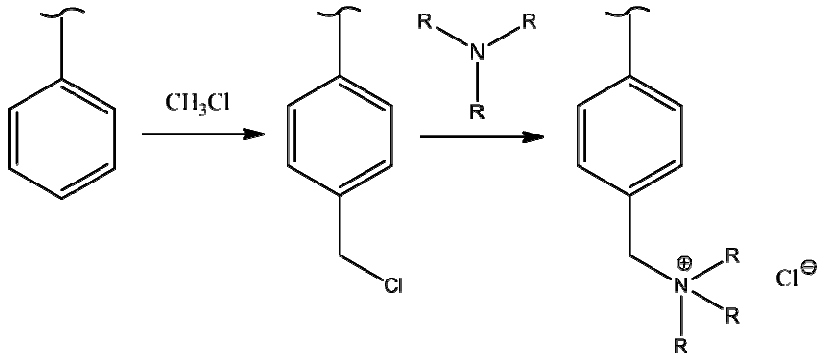


Figure 2.1. Addition of quaternary amine group to polystyrene resin.

Polyacrylic resins are functionalized through the addition of dimethylaminopropylamine (DMAPA). Treatment with methyl chloride produces a positively charged quaternary amine functional group (Figure 2.2) (Harland, 1994).

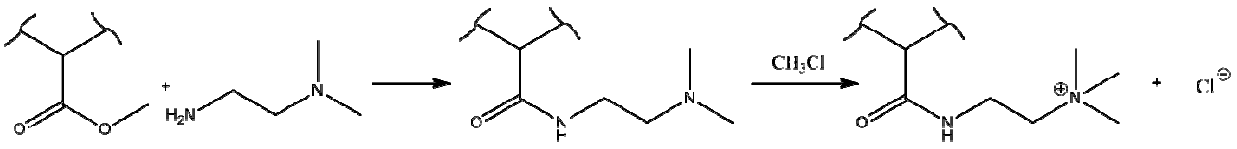


Figure 2.2. Addition of quaternary amine group to polyacrylic resin.

The presence of trialkylamines in the chemical structures of resins and as raw materials for resin synthesis strongly suggests a relationship between anion exchange resins and the potential formation of nitrosamines. DMA is a principal precursor of NDMA, and TMA, DMEA and DMAPA contain the DMA group. Further, TEA, TPA and TBA may have analogous relationships to NDEA, NDPA and NDBA formation.

Early studies found that anion exchange resins used in deionized water systems released NDMA (Fiddler et al., 1977; Gough et al., 1977; Kimoto et al., 1980). More recent studies focusing on nitrosamines as drinking water contaminants found that anion exchange resins used in drinking water treatment released nitrosamines. In what its authors described as a "limited study," four resins, containing DMEA, TMA, TEA and TPA functional groups, were soaked in NaCl and rinsed with deionized water before being contacted with untreated groundwater, distilled water, and distilled water containing nitrite for 3 hours (Najm and Trussel, 2001). The DMEA and TMA resins released appreciable levels of NDMA (up to 140 ng/L). In this preliminary investigation, the releases of NDEA or NDPA by the TEA and TPA resins were not measured, nor were the releases of nitrosamine precursors. In another study (Kemper et al., 2010), a TMA, a TBA and a DMEA resin were found to release NDMA in continuous-flow column experiments (empty bed contact time of 6 minutes) with a model water buffered at pH 8.5 and containing chloride, sulfate and nitrate. The resins were not cleaned in any way prior to the experiments. The resins released high levels of NDMA precursors (1000 - 11,000 ng/L) at the beginning of the flow experiments, but the levels quickly subsided. NDMA precursor levels rose after resins were regenerated with NaCl, and nitrosamine levels

increased considerably when free chlorine or preformed monochloramine was introduced to the feed water. The TBA resin released comparable levels of NDMA and NDBA.

While these studies demonstrated a link between anion exchange resins and nitrosamines, they tended to be limited in scope, each investigating three or four different resins out of the wide array of resins used for drinking water treatment applications. Furthermore, these studies focused on NDMA, but there are three other carcinogenic nitrosamines that may be associated with the use of anion exchange resins. The objective of this study was to investigate the release of NDMA, NDEA, NDPA and NDBA and their precursors by a large, representative group of resins employed for the treatment of drinking water. Sixteen resins with different functional groups, pore structures and polymer matrices from several different manufacturers were subjected to batch contact experiments to determine nitrosamine and nitrosamine precursor release. The effects of pH on nitrosamine and nitrosamine precursor release were also studied. A continuous-flow column study was conducted in follow-up to this batch study and is the subject of another paper.

Materials and Methods

Materials

NDMA, NDEA, NDPA, NDBA, d6-NDMA and d14-NDPA standards were obtained from Accustandard (New Haven, CT) and d10-NDEA and d18-NDBA were obtained from CDN Isotopes (Pointe Claire, Quebec, Canada). EPA Method 521 method-specific activated carbon solid phase extraction (SPE) cartridges were purchased from Restek (Bellefonte, PA). Laboratory-grade water (LGW) was prepared using a system

consisting of filters, granular activated carbon adsorbers, mixed-bed ion exchange resins and ultraviolet (UV) treatment. The LGW was analyzed periodically and found to contain levels of nitrosamines and nitrosamine precursors below detection limits. All other chemicals were purchased from Fisher Scientific (Pittsburgh, PA) and were reagent-grade or higher. All glassware was rendered chlorine demand-free, rinsed with acetone and baked at 400 °C for four hours. Detergent, which often contains TEA, was not used at any time during glassware preparation.

Strong base anion exchange resins were obtained from four different manufacturers. Resin characteristics are presented in Table 2.1. The resins investigated are all commercially available for use in drinking water treatment plants. Of the 16 resins, 5 are TMA resins, 2 are TEA resins, 1 is a TPA resin, 3 are TBA resins, 1 is a TEA/TBA combination resin, and 4 are Type II DMEA resins. Six have gel structures while 10 have macroporous structures. Three have a polyacrylic matrix while 13 have a polystyrene matrix. The resins each came from one batch; possible batch-to-batch differences were not investigated.

Table 2.1. Characteristics of resins investigated.

Resin	Functional Group	Pore Structure	Polymer Matrix
A300E	DMEA	Gel	Styrene
A530E	TEA/TBA	Macroporous	Styrene
A600E	TMA	Gel	Styrene
A860E	TMA	Macroporous	Acrylic
CalRes 2103	TPA	Macroporous	Styrene
CalRes 2109	TBA	Macroporous	Styrene
IRA410	DMEA	Gel	Styrene
IRA910	DMEA	Macroporous	Styrene
MIEX	TMA	Macroporous	Acrylic
PWA15	TMA	Gel	Styrene
PWA2	TBA	Macroporous	Styrene
PWA5	TEA	Macroporous	Styrene
PWA9	TMA	Macroporous	Acrylic
SBG2HP	DMEA	Gel	Styrene
SIR-100	TEA	Macroporous	Styrene
SIR-110	TBA	Gel	Styrene

Initial Resin Cleaning

Immediately prior to use, 200 mL of each resin was loaded into a glass chromatography column (inner diameter 2.5 cm) for cleaning. Resins were subjected to cleaning with 3 bed volumes (BV) of 10% NaCl solution followed by a rinse with 17 BV of LGW at a flow rate of 66.7 mL/min, giving a 3 min empty bed contact time (EBCT). This cleaning procedure was developed based on the recommendations of different resin suppliers for the commissioning of resins for use in water treatment plants. Because column flow was not possible with the MIEX resin due to the small size of the resin

beads, MIEX resin was cleaned by swirling 200 mL of resin in 200 mL of LGW 20 times.

Batch Contact Experiments

The cleaned resins were contacted with LGW at a resin concentration of 20 mg/L. The solutions were buffered at pH 7.0 with a 10 mM phosphate buffer. After 1 hour of contact, the resins were separated from solution using 0.7 µm pore size borosilicate filters that were rinsed with 1.0 L of LGW and baked at 400 °C for four hours. The solutions were then analyzed for nitrosamines and nitrosamine formation potential.

Nitrosamine Analysis

Samples for nitrosamine analysis (1.0 L) were spiked with 50 ng/L d6-NDMA, d10-NDEA, d14-NDPA and d18-NDBA for quantitation by isotope dilution and extracted using activated carbon SPE cartridges. The cartridges were eluted with 30 mL of methylene chloride. LGW (1-2 mL) was added to the extracts and the methylene chloride was removed using a rotary evaporator. The extracts were analyzed by ultra-performance liquid chromatography tandem mass spectrometry in the positive electrospray ionization mode using a Waters Acquity UPLC BEH phenyl column (100 mm x 2.1 mm x 1.7 µm). The mobile phase was composed of a 0.2 mM aqueous formic acid solution and methanol. The percentage of methanol in the mobile phase began at 10% and increased from 10% to 45% from 0 to 4 min and from 45% to 95% from 4 to 6 min, remained at 95% from 6 to 9 min, then decreased from 95% to 10% from 9 to 10 min, remaining at 10% for a 2 min re-equilibration period. Analyte identity confirmation was achieved by comparing retention times and product ion ratios of sample analytes

with those of standards. Mass spectrometry details are summarized in Table 2.2, and further analytical details are included in Appendix A.

Table 2.2 Precursor and product ions for nitrosamine analysis.

Nitrosamine	Precursor Ion	Product Ions	Product Ion Ratio	Collision Voltage
NDMA	75	43/58	0.31	17
d6-NDMA	81	46/64	0.33	17
NDEA	103	75/47	0.056	28
d10-NDEA	113	81	0.90	12
NDPA	131	43/59	0.46	28
d14-NDPA	145	97/127	0.12	11
NDBA	159	103/57	0.12	28
d18-NDBA	177	113/66	0.50	10

Average method recoveries of analytes in LGW were 80.1% for NDMA, 74.8% for NDEA, 81.2% for NDPA and 68.0% for NDBA. Matrix effects were corrected for using isotope dilution with a deuterium-labeled surrogate for each analyte. The limits of quantitation (LOQ), defined as the nitrosamine concentrations that resulted in responses with signal to noise ratios greater than 10, were 4.9 ng/L for NDMA, 1.4 ng/L for NDEA, 3.9 ng/L for NDPA and 1.3 ng/L for NDBA.

Nitrosamine Formation Potential Analysis

Samples (1.0 L or 500 mL) were buffered at pH 6.8 with 20 mM phosphate and dosed with excess preformed monochloramine (140 mg/L NH_2Cl as Cl_2) in accordance with the method described by Mitch et al. (2003). After a 10-day reaction time, samples were quenched with ascorbic acid and analyzed for nitrosamines. Nitrosamine levels measured in identical water samples not treated with monochloramine were subtracted from these levels to obtain the nitrosamine formation potential (NFP) values. This analysis is intended to quantify nitrosamine precursors released from the resins.

Results and Discussion

General Batch Contact Experiments

The anion exchange resins were found to release various amounts of nitrosamines and nitrosamine precursors during 1 hour of contact with water after the vendor-recommended cleaning procedure. Figure 2.3 illustrates the release of nitrosamines during contact experiments at pH 7.These nitrosamines may have been present as impurities in the resins from the manufacturing process or as oxidation products of residual unreacted trialkylamine starting material from resin synthesis.

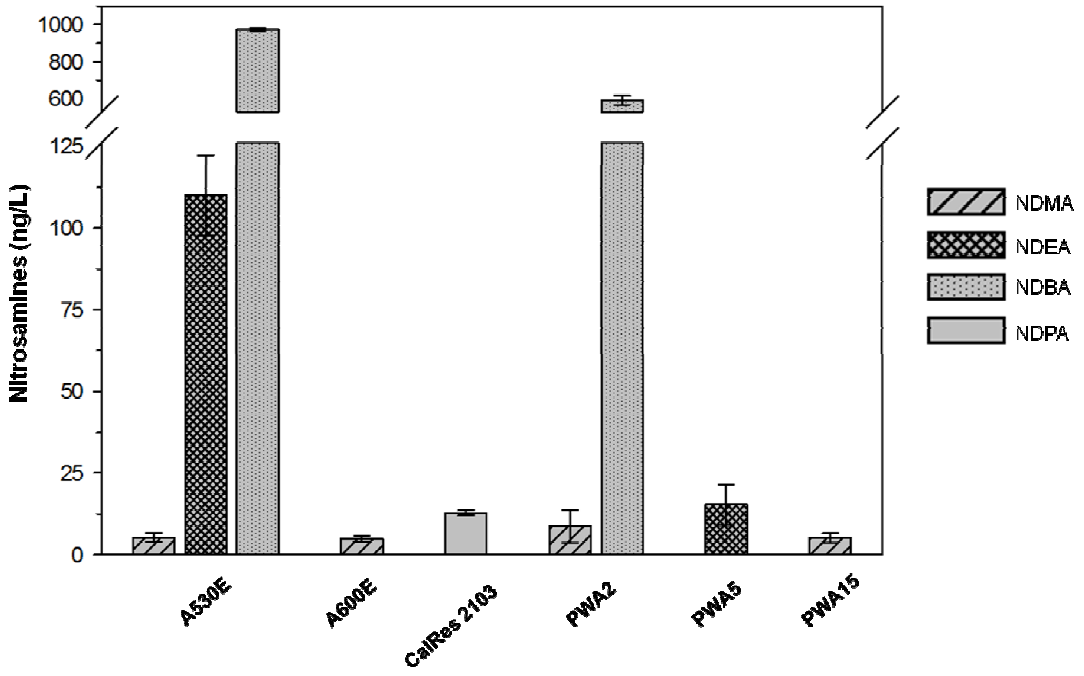


Figure 2.3. Nitrosamines released by selected anion exchange resins during 1 hour contact experiments at pH 7. Error bars indicate one standard deviation where multiple replicate experiments were performed.

NDMA was released at relatively low levels (<10 ng/L) by several of the resins. Resins containing TEA functional groups released levels of NDEA at higher levels (15-

110 ng/L), and resins containing TBA functional groups released NDBA at yet higher levels (592-974 ng/L). The higher releases of NDEA and NDBA can be explained by their different chemical structures. Longer alkyl chains make molecules more hydrophobic, and more hydrophobic molecules are more likely to be trapped in the hydrophobic polymer matrices of the resins during resin formulation. NDBA, with the longest alky chain, can be expected to be retained in the polymer matrix to the greatest extent and is therefore released at the highest concentrations, followed by NDEA and NDMA.

The lone resin containing TPA functional groups (CalRes 2103) released NDPA at 13 ng/L. All of the other resins listed in Table 2.1 but not included in Figure 2.3 were investigated and found to release nitrosamines at levels below the limits of quantitation. Of all the resins tested, 6 out of 16 released nitrosamines at quantifiable levels.

Resin A530E, a bi-functional TEA/TBA resin, released not only NDEA and NDBA, but also NDMA. It is noteworthy that this resin and Resin PWA2, a TBA resin, released NDMA as there are no corresponding TMA of DMA functionalities present in these resins. This NDMA is probably derived from TMA impurities present in the TEA and TBA starting materials used to synthesize the resins. Kemper et al. (2009) reported the release of NDMA by a TBA resin, but found that the resin released comparable amounts of NDMA and NDBA rather than the very different concentrations reported here. Najm and Trussel (2001) reported that TEA and TPA resins released very low levels of NDMA but did not investigate NDEA or NDPA release. In this study, resins containing only TMA functional groups did not release detectable levels of NDEA,

NDPA or NDBA or their precursors. Resin PWA5, a TEA resin, released NDEA but no detectable NDMA.

Figure 2.4 presents the release of nitrosamine precursors by the different anion exchange resins tested during the 1 hour contact experiments at pH 7. These precursors are most likely present as unreacted raw materials from resin synthesis (see Figures 2.1 and 2.2). Unreacted TMA, TEA, TPA or TBA molecules, which are known to be nitrosamine precursors, can remain trapped within the polymer matrix and subsequently released upon prolonged contact with water.

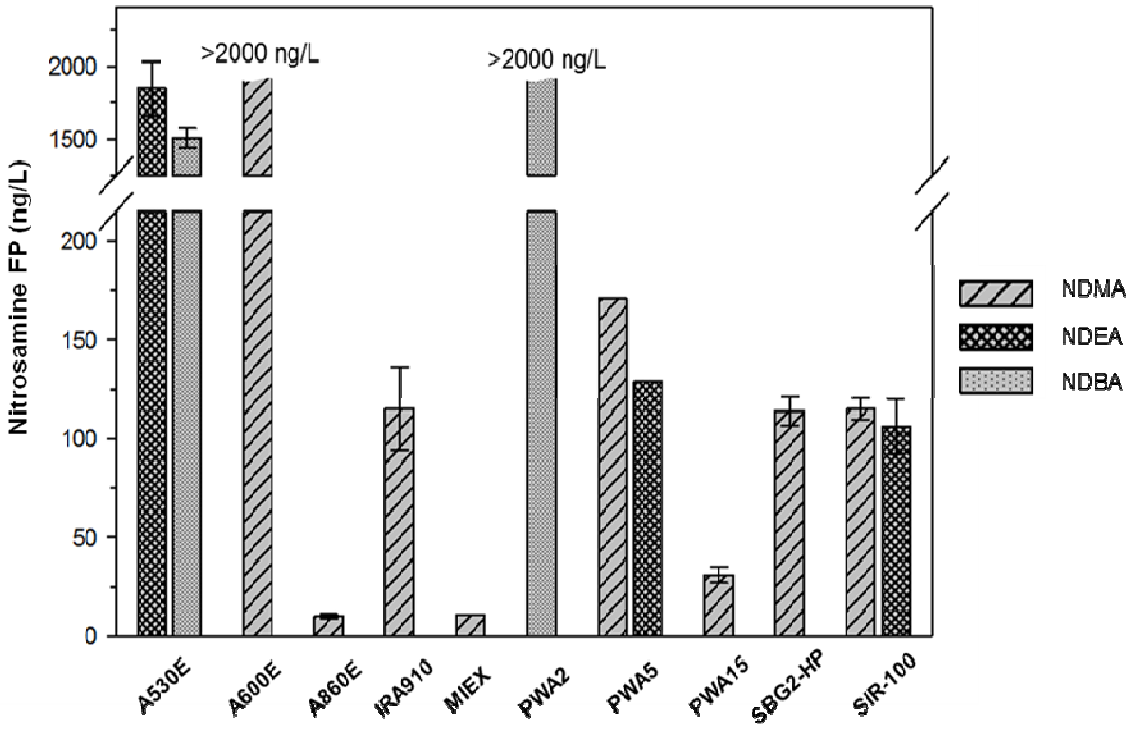


Figure 2.4. Nitrosamine precursors released by anion exchange resins during 1 hour contact experiments at pH 7. Error bars indicate one standard deviation where multiple replicate experiments were performed.

NDMA, NDEA and NDBA precursors were released over a wide range of concentrations, with NDMA and NDBA precursor release in excess of 2000 ng/L (the highest calibration standard injected) and NDEA precursor release reaching 1850 ng/L. Resins that released nitrosamines generally released nitrosamine precursors at appreciably higher levels. Resins A860E, CalRes 2103 and PWA9 released nitrosamine precursors below quantitation limits.

Resin SIR-100, a TEA resin, released NDMA precursors as well as NDEA precursors. Again, this was noteworthy because TEA resin preparation does not include any TMA starting materials that could go unreacted and be released as NDMA precursors. Resin A530E, a bi-functional TEA/TBA resin, and PWA2, a TBA resin, both released NDMA but did not release quantifiable concentrations of NDMA precursors.

pH Batch Contact Experiments

Because pH can affect the extent of charge for any of the residual trialkylamine contaminants associated with any of the resins and is a factor in NDMA formation, the impact of pH on the release of nitrosamines and nitrosamine precursors was investigated. Batch contact experiments were performed on selected resins at various pH levels from pH 4 to 10. Figure 2.5 shows the release of NDMA and NDEA precursors at the various pH values by Resins PWA5, IRA910 and SIR-100, resins which were observed to release noteworthy levels of NDMA and NDEA precursors at pH 7.

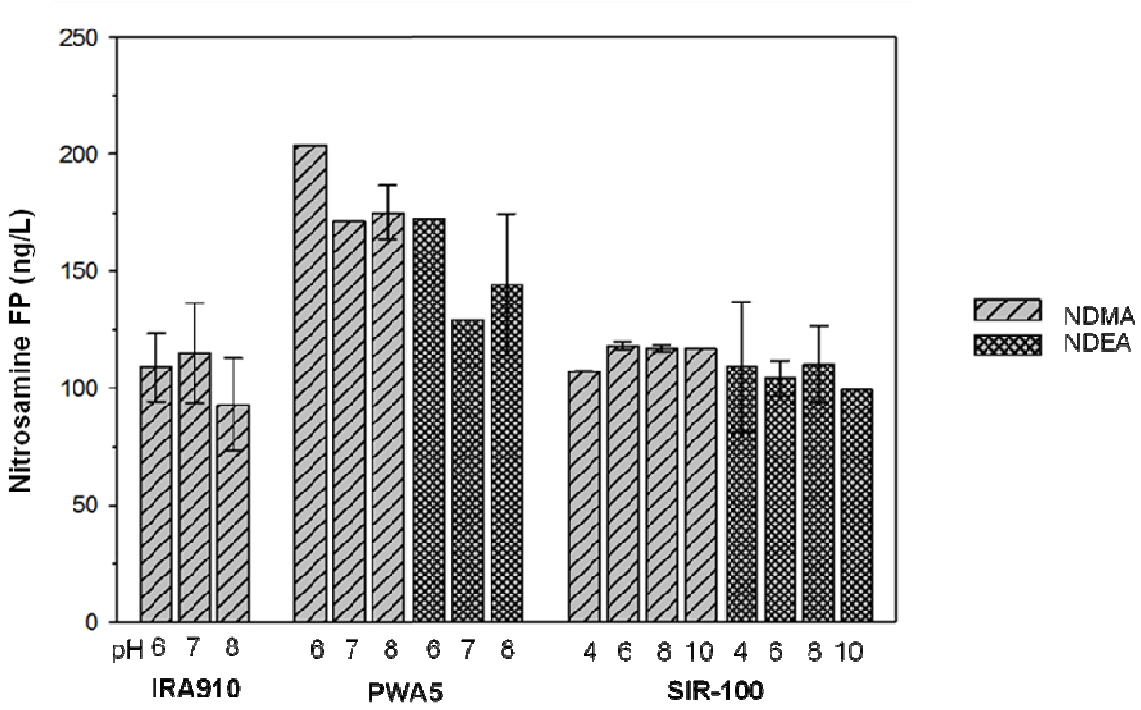


Figure 2.5. Release of NDMA and NDEA precursors at different pH levels.

As illustrated, there was no appreciable difference in NDMA/NDEA precursor release by Resins PWA5 and IRA910 from pH 6 to pH 8, or in NDMA/NDEA precursor release by Resin SIR100 from pH 4 to pH 10.

Summary

The release of nitrosamines by some resins and the release of nitrosamine precursors by many resins among a large, representative group of anion exchange resins used in water treatment practice has been demonstrated and confirmed. The release of multiple nitrosamine precursors by single resins, and the previously unreported release of NDEA and NDEA precursors by TEA resins are significant findings. Of special concern are the high releases of nitrosamines by some resins and the high releases of nitrosamine precursors by several of the resins. Accordingly, it is important to consider the effects of resin-cleaning on nitrosamine and nitrosamine precursor release prior to placing them in

service. It is not possible, using batch experiments, to distinguish between surface contaminants that are easily washed away and precursors embedded within the resin structure that are steadily released over time. Continuous flow-through column experiments with a large, representative group of resins are recommended to further investigate the release of nitrosamines and nitrosamine precursors by anion exchange resins.

Chapter 3. Anion Exchange Resins as Sources of Nitrosamines and Nitrosamine Precursors. II. Simulated Treatment Operations

Introduction

Nitrosamines are a class of highly potent chemical carcinogens that include, among others, N-nitrosodimethylamine (NDMA), N-nitrosodiethylamine (NDEA) and N-nitrosodi-n-butylamine (NDBA). Nitrosamines, especially NDMA, have been detected in a number of drinking waters (Valentine et al., 2006; Charrois et al., 2007; Wang et al., 2011) and are candidates for EPA regulation. NDMA has been identified as a byproduct of the disinfection of drinking water with chloramines (Choi and Valentine, 2002a) and compounds containing dimethylamine (DMA) groups have been identified as important NDMA precursors (Mitch and Sedlak, 2004).

Anion exchange resins are commonly used for the removal of anionic contaminants such as nitrate, perchlorate, arsenic, chromate, and dissolved organic matter during drinking water treatment. These resins consist of crosslinked polymer networks (styrene-divinylbenzene or polyacrylate) functionalized with quaternary amine groups to provide positively charged exchange sites. Exchange site functional groups include trimethylamine (TMA), dimethylethanolamine (DMEA), triethylamine (TEA) and tri-n-butylamine (TBA). TMA and DMEA both contain DMA and can thus react to form NDMA. TEA and TBA have analogous relationships to NDEA and NDBA, respectively. The presence of these trialkylamines in the chemical structures of resins and as raw

materials for resin synthesis strongly suggests a relationship between anion exchange resins and potential formation of nitrosamines.

Recent studies have found that anion exchange resins can serve as sources of nitrosamines and nitrosamine precursors. In a limited study (Najm and Trussel, 2001), four resins were soaked in NaCl, rinsed, and contacted with untreated groundwater, distilled water, and distilled water containing nitrite for 3 hours. Two resins containing TMA and DMEA functional groups released NDMA at concentrations up to 140 ng/L. Nitrosamine precursors and other nitrosamines were not investigated. A more comprehensive study investigated sixteen resins (see Chapter 2). The resins were rinsed with NaCl and laboratory-grade water before being contacted with water at pH 7 for 1 hour. Six of the resins were found to release nitrosamines, with NDMA releases below 9 ng/L, while NDEA levels up to 110 ng/L and NDBA levels as high as 970 ng/L were reported. Ten of the resins were found to release nitrosamine precursors, with NDEA precursor release as high as 1850 ng/L and NDMA and NDBA precursor releases above 2000 ng/L. Resins containing TEA and TBA functional groups were found to release NDMA precursors in addition to TEA and TBA precursors.

It was noted (see Chapter 2) that it is not possible, using batch experiments, to distinguish between surface contaminants that are easily washed away and precursors embedded within the resin structure that may be steadily released over time. They recommended that continuous flow-through column experiments be conducted to more appropriately investigate the release of nitrosamines and nitrosamine precursors by anion exchange resins.

Kemper et al. (2010) conducted bench-scale column studies using a TMA resin, a DMEA resin and a TBA resin. The resins were subjected to a continuous flow of water containing chloride, sulfate and nitrate, buffered at pH 8.5. The resins released low levels of NDMA (rarely above 10 ng/L). The resins released high levels of NDMA precursors (1000 - 11,000 ng/L) at the beginning of the experiments, but the releases quickly subsided. NDMA precursor levels rose again after the resins were regenerated with NaCl, and nitrosamine levels increased considerably when free chlorine or preformed monochloramine was introduced to the feed water. The TBA resin released comparable levels of NDMA and NDBA.

Previous studies have examined small groups of three or four resins, and all but one were limited to batch studies. The objective of this study was to investigate the release of nitrosamines and nitrosamine precursors in flow-through column studies by a large, representative group of resins used for the treatment of drinking water. Fourteen resins with different functional groups, pore structures and polymer matrices from different manufacturers were contacted with a model water in continuous-flow column contact experiments. Treatment plant operations, including regeneration, periodic down-time, and the introduction of low levels of oxidant, were simulated. The initial releases of nitrosamines and nitrosamine precursors, and the effects of these treatment operations on nitrosamine and nitrosamine precursor release, were observed.

Materials and Methods

Materials

NDMA, NDEA, NDBA, and d6-NDMA standards were obtained from Accustandard (New Haven, CT). d10-NDEA and d18-NDBA were obtained from CDN Isotopes (Pointe Claire, Quebec, Canada). EPA Method 521 method-specific activated carbon solid-phase extraction (SPE) cartridges were purchased from Restek (Bellefonte, PA). Laboratory-grade water (LGW) was prepared using a system consisting of filters, granular activated carbon adsorbers, mixed-bed ion exchange resins and UV irradiation treatment. The LGW was analyzed periodically and no nitrosamines or nitrosamine precursors were detected. All other chemicals were purchased from Fisher Scientific (Pittsburgh, PA) and were reagent-grade or higher. All glassware was rendered chlorine demand-free, rinsed with acetone and baked at 400 °C for four hours. Detergent, which often contains TEA, was not used at any time during glassware preparation. To avoid contamination, no rubber was used in the column setup.

Strong base anion exchange resins were obtained from four different manufacturers that provide resins for water treatment practice. Samples of a representative collection of Type I resins with TMA, TEA and TBA functional groups as exchange sites, as well as bi-functional resins using both TEA and TBA and Type II resins with DMEA functional groups, were used in the experiments. The group includes resins with both gel and macroporous pore structures. All of the resins have polymer backbones consisting of styrene crosslinked with divinylbenzene except for A860E, which contains a polyacrylate backbone. Resin characteristics are presented in Table 3.1. Each of these resins is commercially available for use in drinking water treatment plants.

The resins each came from one batch; possible batch-to-batch differences were not investigated.

Table 3.1. Characteristics of resins investigated.

Resin	Functional Group	Pore Structure	Polymer Backbone
A300E	DMEA	Macroporous	Styrene
A400E	TMA	Gel	Styrene
A520E	TEA	Macroporous	Styrene
A530E	TEA/TBA	Macroporous	Styrene
A532E	TEA/TBA	Gel	Styrene
A600E	TMA	Gel	Styrene
A860E	TMA	Macroporous	Acrylic
CalRes 2109	TBA	Macroporous	Styrene
IRA400	TMA	Gel	Styrene
PWA15	TMA	Gel	Styrene
PWA2	TBA	Macroporous	Styrene
PWA5	TEA	Macroporous	Styrene
SIR-100	TEA	Macroporous	Styrene
SIR-110	TBA	Gel	Styrene
TAN-1	TMA	Macroporous	Styrene

Continuous-flow Column Contact Experiments

Resins (200 mL bed volume (BV)) were packed into glass chromatographic columns with an inner diameter of 2.5 cm. LGW containing 10 mM phosphate buffer at pH 7 was passed through the columns at a flow rate of 66.7 mL/min, resulting in an empty bed contact time (EBCT) of 3 min. This EBCT is typical of contact times used for ion exchange in water treatment practice. The columns were regenerated periodically

with 600 mL (3 BV) of a 10% NaCl solution. Column flow was interrupted periodically and the resins were stored submerged in the columns for 12-14 hours. Feed water containing free chlorine (0.24 mg/L as Cl_2) or preformed monochloramine (0.24 mg/L as Cl_2) was introduced at the end of each experiment. At the conclusion of each experiment, the resin was removed from the column and discarded, and the column was cleaned with nitric acid and acetone and rinsed with LGW before being packed with a new resin.

Samples (2.0 L, 10 BV) were collected at the beginning of each column experiment and immediately before and after regenerations, flow interruptions and the introduction of oxidant, and were analyzed for nitrosamines and nitrosamine precursors.

Nitrosamine Analysis

NDMA, NDEA and NDBA were analyzed as previously reported (see Chapter 2). Briefly, samples were spiked with 50 ng/L d6-NDMA, d10-NDEA, and d18-NDBA for quantitation by isotope dilution before being concentrated with activated carbon SPE cartridges and eluted with methylene chloride. LGW was added to the extracts and methylene chloride was removed using a rotary evaporator. The extracts were analyzed by ultra performance liquid chromatography – tandem mass spectrometry (UPLC-MS/MS). Limits of quantitation (LOQ) were 4.9 ng/L for NDMA, 1.4 ng/L for NDEA and 1.3 ng/L for NDBA.

Nitrosamine Formation Potential Analysis

Nitrosamine precursors were analyzed as previously reported (see Chapter 2) following the method described by Mitch et al. (2003). Briefly, samples were reacted with a large excess of preformed monochloramine for 10 days, after which they were analyzed for nitrosamines as described above.

Results and Discussion

Illustrative Results

Illustrative results of a continuous-flow column contact experiment with Resin A300E, a Type II DMEA resin, are presented in Figures 3.1 and 3.2. Figure 3.1 presents NDMA released, while Figure 3.2 shows the release of NDMA precursors.

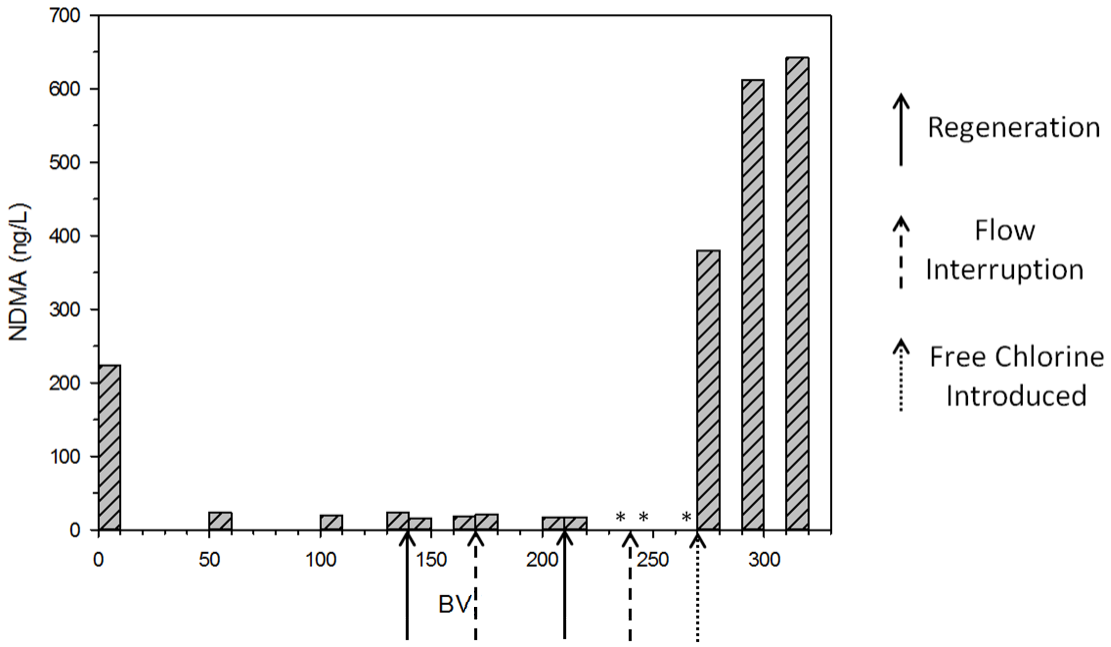


Figure 3.1. NDMA release by Resin A300E during a typical continuous-flow column experiment. (* Indicates that a sample was taken and nitrosamines were below the LOQ.)

Figure 3.1 shows that the first 10 BV of water that passed through the resin contained a high level of NDMA – 223 ng/L. NDMA concentrations dropped considerably as more water was passed through the resin, and the second sample collected, at 50 BV, contained 23 ng/L, much lower than the initial flush but still significant from a potential regulatory or public health standpoint. NDMA concentrations

remained at a similar level, even after two regenerations, and it was not until 240 BV of water was processed that NDMA levels dropped below the LOQ of 4.9 ng/L. There was no apparent increase in NDMA levels as a result of regeneration or from the two 12-14 hour flow interruptions. When feed water containing 0.24 mg/L free chlorine was introduced, NDMA levels rose dramatically, reaching 380 ng/L within the first 10 BV and 642 ng/L within 50 BV. Column effluent contained the same free chlorine concentration as column feed water. No further samples were collected.

Figure 3.2 presents NDMA precursors released during the same continuous-flow column experiment. With respect to NDMA formation potential, the first 10 BV of water that passed through the resin contained a high level of NDMA precursors – 1402 ng/L. Precursor levels, like NDMA levels, fell quickly, with the sample collected at 50 BV containing 34 ng/L. In contrast to the findings for NDMA itself, NDMA precursor levels increased as a result of regeneration and flow interruption. The first regeneration resulted in an NDMA precursor increase of 50 ng/L while the second regeneration resulted in no apparent increase. The first 12-14 hour flow interruption resulted in an NDMA precursor increase of 378 ng/L and the second 12-14 hour flow interruption resulted in a precursor increase of 103 ng/L. In each case, the increased levels of NDMA precursors caused by regeneration or flow interruption subsided within 40 BV. While the introduction of 0.24 mg/L free chlorine resulted in a dramatic increase in NDMA (see Figure 3.1), it did not result in an increase in NDMA precursors.

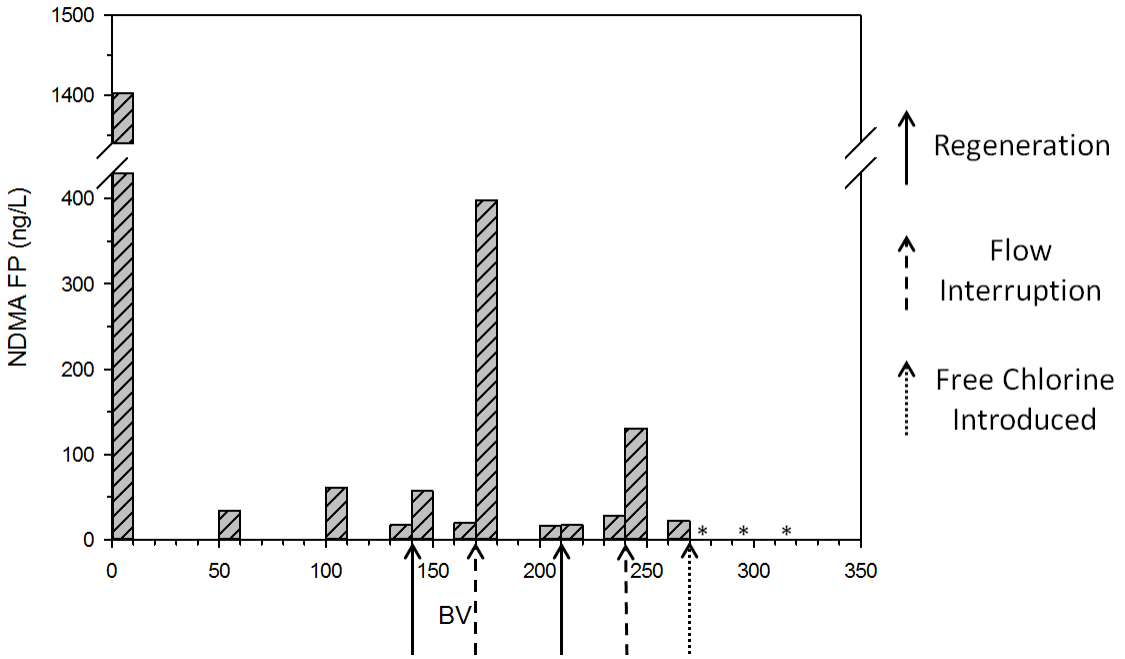


Figure 3.2. NDMA precursor release by Resin A300E during a typical continuous-flow column experiment. (* Indicates that a sample was taken and nitrosamine formation potentials were below the LOQ.)

The results of a continuous-flow column experiment with Resin A530E, a bi-functional TEA/TBA resin, are presented in Figures 3.3 and 3.4 to illustrate findings for the other functional groups. NDBA release was high in the first 10 BV (1300 ng/L) and NDEA release was appreciable (33 ng/L). NDMA was also present at high levels (130 ng/L) in the first 10 BV, even though the resin did not contain any TMA functionality. NDMA levels dropped immediately, with no quantifiable NDMA detected after 50 BV. NDBA was persistent, remaining above 600 ng/L through 100 BV before decreasing to 209 ng/L, still an appreciable level, at 140 BV. NDEA levels remained between 30 and 70 ng/L throughout the first 140 BV. Regeneration did not lead to any increase in NDMA, but caused a decrease in the concentrations of NDEA and NDBA. A 12-14 hour

flow interruption led to appreciable increases of 208 ng/L for NDEA and 640 ng/L for NDBA, but no increase in NDMA.

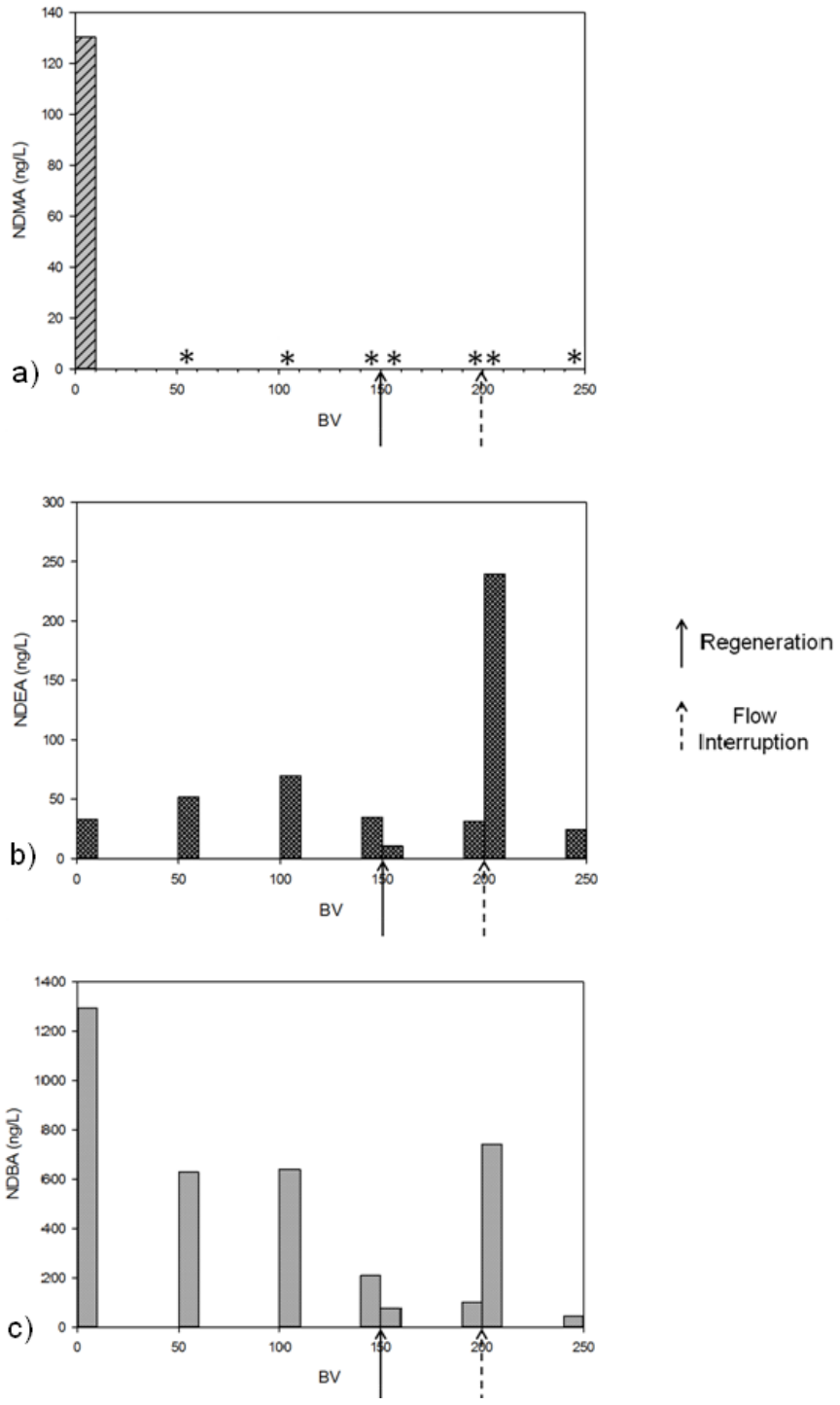


Figure 3.3. Nitrosamine release by Resin A530E during a typical continuous-flow column experiment. a) NDMA release; b) NDEA release; c) NDBA release (* Indicates that a sample was taken and nitrosamine formation potentials were below the LOQ.)

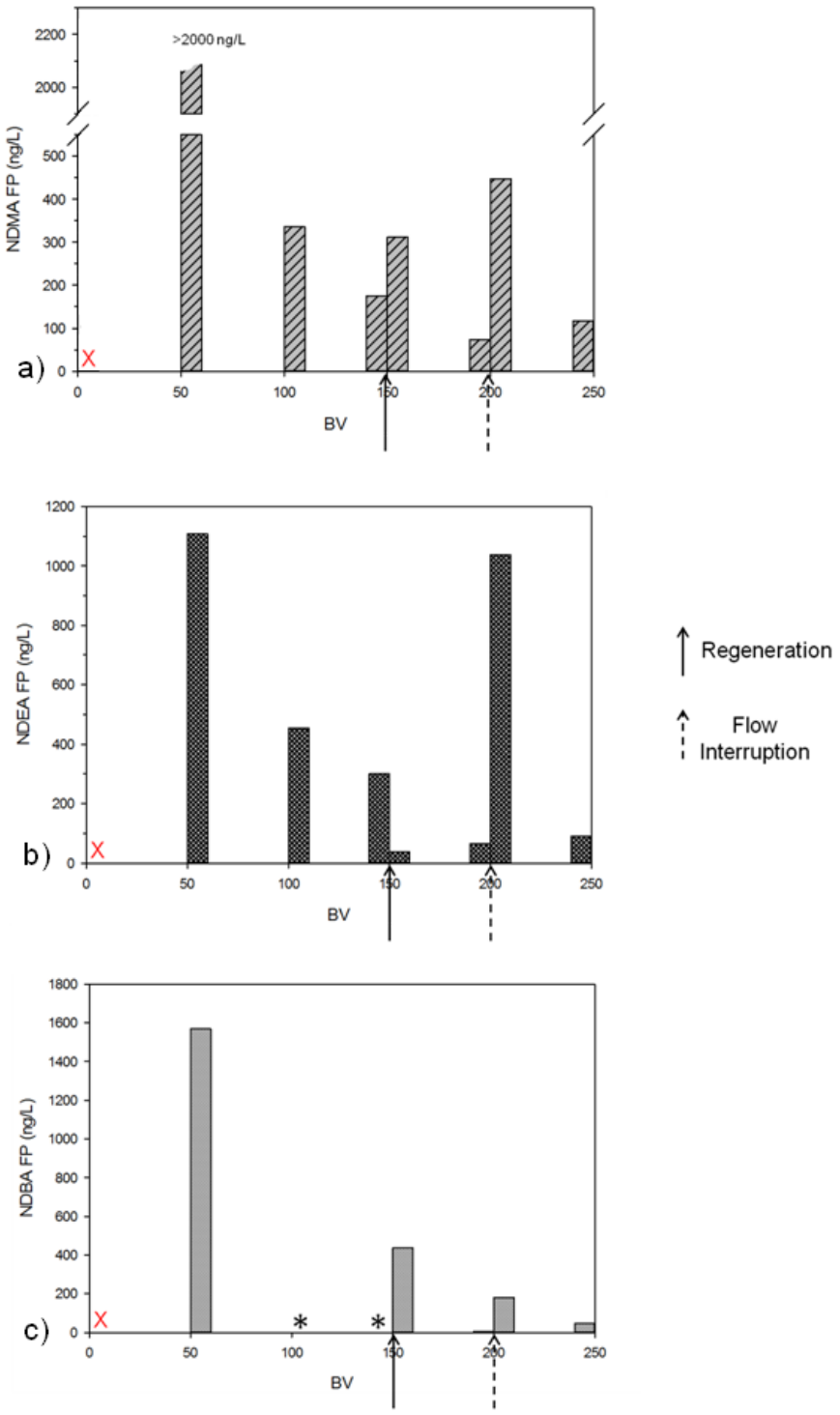


Figure 3.4. Nitrosamine precursor release by Resin A530E during a typical continuous-flow column experiment. a) NDMA precursor release; b) NDEA precursor release; c) NDBA precursors release. (* Indicates that a sample was taken and nitrosamine formation potentials were below the LOQ. X indicates that a sample was lost during processing.)

While the sample collected in the first 10 BV of water that passed through the resin was lost, the water passed through the column from 50 – 60 BV contained high levels of NDEA and NDBA precursors (1108 and 1569 ng/L, respectively), and even higher levels of NDMA precursors (>2000 ng/L, the highest calibration point used), despite the fact that this resin did not contain TMA functional groups. The concentration of NDBA precursors appeared to be lowered to non-detectable levels with continued flow. However, while their concentrations decreased over time, NDMA and NDEA precursors continued to leach from the resin. Regeneration caused an increase in NDMA and NDBA precursor levels but not for NDEA precursors, and the 12-14 hour flow interruption resulted in an increase in precursor levels for all three nitrosamines.

Additional Investigations

Resins A530E and PWA5 were subjected to ten successive regenerations in additional column experiments. Results (see Appendix B) indicated that nitrosamine precursor release decreased with repeated regenerations.

Column experiments were performed with Resins PWA5 and TAN-1 immediately after receipt of resin samples and after six months of storage in the dark at 4°C to test the stability of the resin during storage. Results were inconclusive, as Resin PWA5 released appreciably increased levels of both NDMA and NDEA precursors after six months, while Resin TAN-1 released comparable levels in both experiments (see Appendix B).

Reproducibility

To investigate the reproducibility of the experimental procedure, three identical column experiments were performed with Resin PWA15. The results of these

experiments are included in Appendix C. None of the samples collected during these experiments contained quantifiable levels of nitrosamines themselves, although they did contain appreciable levels of nitrosamine precursors. NDMA precursor levels measured in samples collected before and after regeneration and before and after the 12-14 hour flow interruption agreed with each other within a relative standard deviation of 30%. The initial 10 BV replicate samples exhibited large standard deviations, but they were reproducible in that they all showed high NDMA formation potentials. An explanation for the high standard deviations among the first 10 BV replicates is given in Appendix C.

Summary of Results for all Resins Tested

Column experiments similar to those illustrated above were performed with each of the resins listed in Table 3.1. The results for the other resins are presented in Appendix D. Seven of the fourteen resins investigated released quantifiable levels of nitrosamines in the first 10 BV of flow. These nitrosamines are probably present as impurities from the resin synthesis process, as suggested by Kemper et al. (2010) and in Chapter 2. In each case, elevated levels of nitrosamine release dropped to low ng/L levels within 100 BV of flow. Resin A530E was the only resin to release elevated levels of nitrosamines after regeneration and flow interruption (see Figure D.7).

The release of nitrosamine precursors was more interesting. Table 3.2 presents the release of NDMA precursors by resins with TMA and DMEA functional groups in the first 10 BV, due to regeneration, and due to flow interruption. Table 3.3 presents the release of NDMA, NDEA and NDBA precursors by resins with TEA or TBA functional groups and by TEA/TBA bi-functional resins.

Table 3.2. NDMA precursor release by TMA and DMEA resins during continuous-flow column experiments.

			First 10 BV	Regeneration Effect	Flow Interruption Effect
Resin	**Functional Group**	**Pore Structure**	**NDMA FP (ng/L)**	**NDMA FP (ng/L)**	**NDMA FP (ng/L)**
IRA400	TMA	Gel	>2000	269	>2000
A600E	TMA	Gel	>2000	184	>2000
A400E	TMA	Gel	1880	19	442
A860E	TMA	Macroporous	>2000	<1.4	400
PWA15	TMA	Gel	333	<1.4	821
TAN-1	TMA	Macroporous	165	16	54
A300E	DMEA	Gel	1400	50	380

Table 3.3. NDMA, NDEA and NDBA precursor release by TEA, TBA and bi-functional TEA/TBA resins during continuous-flow column experiments.

			First 10 BV			Regeneration Effect			Flow Interruption Effect		
			NFP (ng/L)			NFP (ng/L)			NFP (ng/L)		
Resin	**Functional Group**	**Pore Structure**	**NDMA**	**NDEA**	**NDBA**	**NDMA**	**NDEA**	**NDBA**	**NDMA**	**NDEA**	**NDBA**
A530E	TEA/TBA	Macro	>2000	>1000	>1000	136	<1.4	157	380	974	176
A532E	TEA/TBA	Gel	431	>2000	38	x**	x	x	959	12	>2000
CalRes 2109	TBA	Macro	<4.9	na*	>2000	<4.9	na	<1.3	<4.9	na	<1.3
PWA2	TBA	Macro	328	na	113	<4.9	na	<1.3	<4.9	na	<1.3
SIR-110	TBA	Gel	>2000	na	60	<4.9	na	20	<4.9	na	5
A520E	TEA	Macro	>2000	>2000	na	<4.9	<1.4	na	1340	>2000	na
PWA5	TEA	Macro	300	400	na	67	<1.4	na	48	120	na
SIR-100	TEA	Macro	130	300	na	<4.9	<1.4	na	x	x	x

***na (not applicable) indicates that the resin was not expected to release precursors of the indicated nitrosamine and did not release such precursors at a quantifiable level.**
****x indicates that the sample was lost during processing and analysis.**

All of the resins released high levels of nitrosamine precursors in the first 10 BV. Trialkylamines are used as reagents in resin synthesis (Kunin, 1963; see Chapter 2), and unreacted trialkylamine starting materials likely account for the observed release of

nitrosamine precursors. Precursor release typically dropped to low ng/L levels within 100 BV of column throughput.

It is noteworthy that TEA, TBA and bi-functional TEA/TBA resins also released NDMA precursors (see Table 3.3). TEA and TBA are used as starting materials during synthesis of these resins; thus they are likely the sources of the NDEA and NDBA formation potential. These trialkylamines are not expected to react with preformed monochloramine to form NDMA as TMA does. However, commercial trialkylamines have been shown to contain trialkylamines of differing alkyl chain lengths as impurities (de Zeeuw, 2011). The presence of TMA as an impurity in TEA and TBA likely accounts for the NDMA formation potential observed. No TMA resins released quantifiable levels of NDEA or NDBA or their precursors.

In general, NDMA precursors were washed away more quickly than NDEA or NDBA precursors when multiple nitrosamine precursors were released. This illustrates the ability of the resins to act as reverse-phase chromatographic media. The NDMA precursors have shorter carbon chains and so are less hydrophobic in nature and, accordingly, were not retained in the columns. In contrast, NDEA and NDBA precursors have longer carbon chains and are more hydrophobic, causing them to be retained by the resins and released at a slower rate

Regeneration of the resins with 3 BV of 10% NaCl produced an immediate spike in nitrosamine precursor release in seven of the fourteen resins tested. Following this spike, precursor levels returned to low ng/L levels within 20 BV of throughput. The following explanation might account for this behavior. Resins are shipped in the chloride form, i.e. with Cl^- as the counterion, and are designed to selectively exchange these Cl^-

counterions for specific contaminants such as NO_3^-. The resins need to equilibrate with all anions in solution and, in this controlled laboratory study, had the potential to take up $H_2PO_4^-$ and HPO_4^{2-} to some degree when contacted with the pH 7 buffered water, according to Equation 3.1,

$$\underline{Cl^-} + X^-_{(aq)} \leftrightarrow \underline{X^-} + Cl^-_{(aq)} \qquad (3.1)$$

where the underlined terms refer to the resin phase and X^- is $H_2PO_4^-$ or HPO_4^{2-} . When concentrated NaCl is introduced to the column as feed water during regeneration, the equilibrium is pushed back to the left and the resins return to the chloride form. The moisture content of a resin changes as a function of the ionic form of the resin (Montgomery Watson Harza, Inc., 2005). The change in swelling that the resins undergo due to changes in moisture content may cause the polymer matrix to release unreacted trialkylamines that are trapped within the polymer structure, resulting in the increase in nitrosamine precursors observed as a result of regeneration. That there was no increase in nitrosamine release as a result of regeneration suggests that any nitrosamines present as impurities existed on the surface of the resins and were fully washed away before regeneration, while the residual trialkylamine precursors are also embedded within the polymer backbone of the resins. The results from the column studies in which resins underwent repeated regeneration (see Appendix B) indicated that nitrosamine precursors that might be embedded within the resin are ultimately washed out over time. Equation 3.1 applies in water treatment practice as well, where X^- can be nitrate, perchlorate, etc. Hence, nitrosamine precursors can be expected to be released during water treatment practice when the resins are regenerated, due to changing moisture content of the resins and different swelling behavior. Each resin has a different structure and can therefore be

expected to undergo different changes in swelling. Because macroporous resins are rigid and highly crosslinked while gel resins are looser, the two types of resins were expected to behave differently with respect to nitrosamine and nitrosamine precursor release, with gel resins possibly exhibiting greater swelling changes during regeneration, leading to higher releases. However, no discernable differences between the behaviors of the two types of resins were observed.

When flow was interrupted for 12-14 hours and resins were allowed to sit in prolonged contact with the water, there was typically an elevated level of nitrosamine precursors released in the first 10 BV of throughput after flow resumed. During the extended contact time of the flow interruption, water is able to more fully penetrate the polymer backbone of the resins and any residual trialkylamine precursors held within the polymer structure enters the aqueous phase, resulting in the increased levels of nitrosamine precursors observed. Tables 3.2 and 3.3 indicate that, in most cases, nitrosamine precursors in the first 10 BV of flow were higher than levels released after flow interruption, which were in turn higher than those released after regeneration. This suggests that most of the unreacted residual trialkylamine precursor material is at or near the surface of the resins and is rinsed away more quickly.

The bi-functional TEA/TBA resins tended to release higher levels of nitrosamine precursors than did the resins containing only TEA or TBA. TBA resins released NDMA and NDBA precursors in the first 10 BV but did not release any precursors upon flow interruption or regeneration.

Impact of Oxidants

Effluent nitrosamine concentrations rose upon the addition of 0.24 mg/L of preformed monochloramine to the feed water. Table 3.4 presents the levels of nitrosamines released in the first 10 BV after the introduction of monochloramine. All but one of the eight resins contacted with monochloramine produced increased levels of nitrosamines in the first 10 BV of column throughput. None of the resins showed an increase in the levels of nitrosamine precursors.

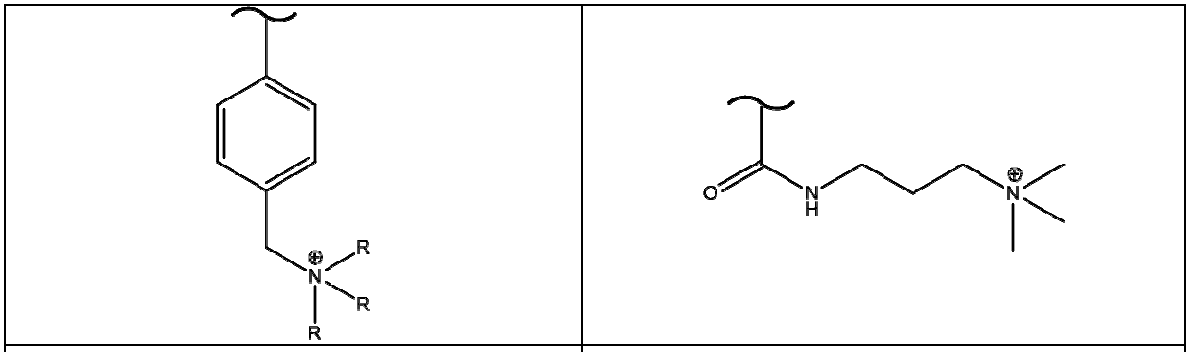
Table 3.4. Nitrosamines in first 10 BV after introduction of monochloramine to feedwater.

Resin	Functional Group	Pore Structure	NDMA (ng/L)	NDEA (ng/L)	NDBA (ng/L)
A400E	TMA	Gel	23	<10	na*
A520E	TEA	Macro	245	<10	na
A600E	TMA	Gel	160	na	na
A860E	TMA	Macro	<4.9	na	na
IRA400	TMA	Gel	847	na	na
PWA2	TBA	Macro	1240	na	212
PWA15	TMA	Gel	123	na	na
SIR-100	TEA	Macro	80	<10	na

***na (not applicable) indicates that the resin was not expected to release precursors of the indicated nitrosamine and did not release such precursors at a quantifiable level.**

Previous studies (Schreiber and Mitch, 2006) have shown that tertiary amines react to form nitrosamines through electrophilic attack of the lone electron pair on the amine by dichloramine, which exists in equilibrium with monochloramine. It has been suggested that quaternary amines in water treatment polymers undergo a Hofmann elimination reaction to become tertiary amines with a lone electron pair available for attack (Park et al., 2009). All of the resins investigated in this study contain styrene-

divinylbenzene polymer backbones except for Resin A860E, which contains a methylacrylate polymer structure. The general structures of the resins are given in Figure 3.5.



Styrene-divinylbenzene Resins	Polyacrylic Resins

Figure 3.5. General chemical structures of styrene-divinylbenzene and polyacrylic resins.

The structure of the polystyrene resins is expected to be chemically stable as there is no lone electron pair available on the amine for electrophilic attack and the proximity of the phenyl group to the amine precludes Hofmann elimination. However, trialkylamines are known to contain dialkylamines as impurities (SigmaAldrich, 2011). If dialkylamine impurities are incorporated into the resin structure as trialkylamines are during resin synthesis, these dialkylamine sites, with their lone electron pairs, will be reactive. Upon chloramination, these sites can undergo electrophilic attack, leading to the release of dialkylamines through hydrolysis of the imine intermediate (Park et al., 2009). These dialkylamines can then react to form nitrosamines (Schreiber and Mitch, 2006). The proposed reaction pathway is shown in Figure 3.6.

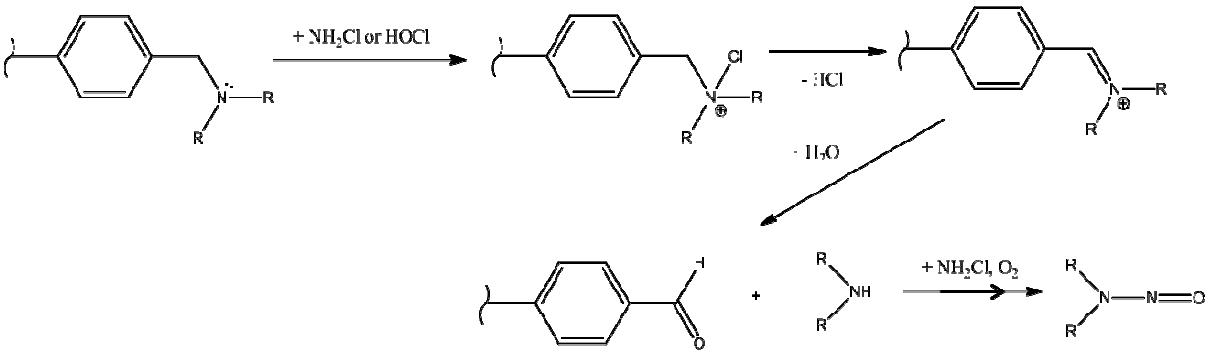


Figure 3.6. Proposed pathway for formation of nitrosamines from dialkylamine groups bound to polystyrene-divinylbenzene polymers.

The dialkylamines released are detected as nitrosamines, rather than as precursors, most likely because there is sufficient monochloramine in the feed water to react with them and convert them to nitrosamines prior to analysis. This does not agree with the findings of Kemper et al. (2010), who observed an increase in nitrosamine precursors when resins were contacted with monochloramine. As noted above, TEA and TBA resins were found to be sources of NDMA. This suggests that DMA, in addition to TMA, is an impurity in the TEA and TBA used in resin synthesis.

Resin A860E, the lone polyacrylic resin, did not produce any detectable nitrosamines upon contact with monochloramine. This is surprising, because polyacrylic resins are synthesized using dimethylaminopropylamine, which contains DMA, the most direct NDMA precursor.

Nitrosamine levels in the column effluent also rose upon the addition of 0.24 mg/L free chlorine to the feed water. Table 3.5 presents the levels of nitrosamines released in the first 10 BV after the introduction of free chlorine.

Table 3.5. Nitrosamines in first 10 BV after introducing free chlorine to feedwater.

Resin	Functional Group	Pore Structure	NDMA (ng/L)	NDEA (ng/L)	NDBA (ng/L)
A300E	DMEA	Gel	380	na	na
A530E	TEA/TBA	Macro	<4.9	<1.4	30
A532E	TEA/TBA	Gel	34	<1.4	<1.3
A600E	TMA	Gel	<4.9	na	na
A860E	TMA	Macro	<4.9	na	na
CalRes 2109	TBA	Macro	31	na	<1.3
IRA400	TMA	Gel	<4.9	na	na
PWA2	TBA	Macro	<4.9	na	<1.3
PWA5	TEA	Macro	75	<1.4	na

***na (not applicable) indicates that the resin was not expected to release precursors of the indicated nitrosamine and did not release such precursors at a quantifiable level.**

Of the resins contacted with free chlorine, five out of nine produced increased levels of nitrosamines and none produced increased concentrations of nitrosamine precursors. As with monochloramine, free chlorine can attack dialkylamine groups and cause them to be released from resin polymers. Because free chlorine is not expected to convert the dialkylamine precursors to nitrosamines, as is the case with chloramines, the dialkylamines released are expected to be observed as precursors rather than as nitrosamines. However, increases in nitrosamines themselves were observed after the introduction of free chlorine. These observations remain unexplained. In general, nitrosamine levels produced by monochloramine were much higher than those produced by free chlorine.

Summary

The levels of nitrosamines and nitrosamine precursors released at the start of the experiments indicate that anion exchange resins tend to be contaminated with impurities as they are received from suppliers. While the impurities appear to be washed away

relatively quickly, the spikes in precursor levels after regeneration and flow interruption leading to prolonged contact times raise concern that drinking waters treated with anion exchange resins may experience periodic increases in nitrosamine levels that occur for extended periods of time. The increase in nitrosamine levels observed when oxidants such as free or combined chlorine were introduced to the feed waters, even at relatively low concentrations, clearly illustrate the need to prevent any chlorine from entering the anion exchange resin vessels. While most nitrosamine research has been focused on NDMA, the release of NDEA and NDBA precursors by several of the resins suggests that the occurrence and behavior of these other nitrosamines are deserving of further investigation.

Chapter 4. The Impact of Anion Exchange Treatment on Nitrosamine and Nitrosamine Precursor Concentrations in Full-Scale Drinking Water Treatment Plants

Introduction

Nitrosamines are a class of highly potent chemical carcinogens and include, among others, N-nitrosodimethylamine (NDMA), N-nitrosodiethylamine (NDEA), and N-nitrosodi-n-butylamine (NDBA). NDMA, the most thoroughly studied and most commonly detected nitrosamine, has been identified as a byproduct of the disinfection of water with chloramines (e.g. Choi and Valentine, 2002a). NDMA, NDEA and NDBA have been detected in a number of drinking waters (Valentine et al., 2006; Charrois et al., 2007; Zhao et al., 2007; Asami et al., 2009; Wang et al., 2011). Nitrosamines are regulated in drinking water in California with notification levels of 10 ng/L (CA DPH, 2008) and are candidates for Federal EPA regulation (USEPA, 2011b).

The presence of nitrosamines in finished drinking water has been linked to the use of anion exchange resins for treatment. Dimethylamine (DMA) has been identified as a key precursor of NDMA (Choi and Valentine, 2002b), and diethylamine (DEA) and di-n-butylamine (DBA) have been shown to have analogous relationships to NDEA and NDBA (Wang et al., 2011). Anion exchange resins have trialkylamine groups such as trimethylamine (TMA), dimethylethanolamine (DMEA), triethylamine (TEA) or tri-n-butylamine (TBA) bound to a polymer backbone as positively charged anion exchange

sites. TMA has been shown to degrade to DMA and further react to form NDMA (Lee et al., 2007), and it is likely that DMEA, TEA and TBA exhibit similar behaviors.

The link between anion exchange and nitrosamines has been demonstrated in the laboratory. Four resins having different functional groups were soaked in NaCl, rinsed, and contacted with water for 3 hours, and the resins containing TMA and DMEA released up to 140 ng/L NDMA (Najm and Trussel, 2001). A more comprehensive study (see Chapter 2) contacting 16 resins with buffered water after an NaCl rinse found that TMA and DMEA resins released NDMA and NDMA precursors. TEA and TBA resins released NDEA and NDBA and their precursors, respectively, while also releasing NDMA and NDMA precursors. Of the sixteen resins investigated in that study, six released notable levels of nitrosamines and ten released appreciable levels of precursors, with nitrosamine releases as high as 1000 ng/L and precursor releases reaching more than 2000 ng/L.

Continuous-flow bench-scale column experiments have yielded insights into the release of nitrosamines and their precursors under simulated treatment conditions. In one study (Kemper et al., 2010), three resins were contacted with water buffered at pH 8.5. The resins released high levels of NDMA precursors (1000 – 11,000 ng/L) at the start of the experiments, with noticeable spikes in precursor levels after simulated regeneration with NaCl. Nitrosamine levels increased considerably when free chlorine or preformed monochloramine was introduced to the feed water. An expanded continuous-flow column study (see Chapter 3) found that thirteen of fourteen resins investigated released high levels of nitrosamine precursors (from 130 ng/L to over 2000 ng/L) in the first 10 bed volumes of flow. Nitrosamine precursor levels rose dramatically in the first 10 bed

volumes after NaCl regeneration and after water stood in the columns during a 12-14-hour flow interruption. The introduction of monochloramine to the feed water caused elevated nitrosamine release. All resins, regardless of their functional groups or structure, released NDMA precursors, and TEA and TBA resins additionally released precursors of the corresponding nitrosamines, NDEA and NDBA.

Anion exchange has been previously identified as a contributory factor for the presence of nitrosamines in finished drinking waters. A study of 21 drinking water treatment plants (Valentine et al., 2006) found that a plant using anion exchange and chlorination had the highest NDMA levels (10-30 ng/L) in its finished water. That study included one other plant employing anion exchange to treat a portion of its water, but the finished water at this plant did not contain elevated NDMA levels. A survey conducted by the California Department of Health Services (CDHS) investigated NDMA in four plants using anion exchange (CDHS, 2002). One of the four plants had elevated NDMA concentrations (30-34 ng/L) in its finished water.

While these studies suggested a link between anion exchange use and the presence of nitrosamines in drinking water, they tended to be limited in scope, and only one investigated NDMA precursors. Furthermore, while these studies focused on NDMA occurrence, there are other nitrosamines that may have relationships to anion exchange resins commonly used in the field, namely NDEA and NDBA. Additionally, the studies measured overall plant influent and effluent, only isolating the anion exchange process in one instance. Accordingly, the objective of this research was to investigate the effect of anion exchange treatment on levels of NDMA, NDEA and NDBA and their precursors in a select sampling of drinking water treatment plants using anion exchange. Ten drinking

water treatment plants, using a total of nine different anion exchange resins for the removal of various contaminants under differing conditions, were identified for sampling. Samples of anion exchange process influent and effluent were taken to isolate the release of nitrosamines and their precursors by the anion exchange resins.

Materials and Methods

Approach

Previous research has identified resins that released high levels of nitrosamines and precursors during bench-scale experiments (see Chapters 2 and 3). Accordingly, full-scale drinking water treatment plants using these resins of interest were identified for sampling. As precursor levels were shown in the laboratory to increase after resin regeneration, samples were taken immediately before and after regeneration in those facilities at which regenerable resins were used. To corroborate laboratory findings that prolonged contact time results in an increase in nitrosamine precursor levels, water that had been sitting in a resin vessel for several months was sampled. Additionally, sample sites were selected to assess the impact of resin age, i.e. how long the resins had been in place since they were first installed. In selecting sampling sites, consideration was given to geographical diversity, i.e. eastern US, midwest, and west coast. Descriptive information about the sampling sites is presented in Table 4.1.

Table 4.1. Summary of sampling sites.

Site	Resin	Resin Functional Group	Target Contaminant	Installation Date	Sampling Date
1	A300E	DMEA	Nitrate	March 2001	April and Aug 2011
2	A300E	DMEA	Nitrate	Feb 2006	July 2011
3	CalRes 2109	TBA	Perchlorate	Nov 2009/July 2010	July 2011
4	A532E	TEA/TBA	Perchlorate	Dec 2010/Jan 2011	Aug 2011
	A520E	TEA	Nitrate	March 2010/Jan 2005	
5	A530E	TEA	Nitrate	2001	June 2011
6	PWA2	TBA	Perchlorate	Feb 2010	Aug 2011
	SIR-100	TEA	Nitrate	June 2008	Oct 2011
7	A860	TMA	NOM	April 2009	March 2011, Aug 2011
8	IRA400	TMA	Nitrate	1992	Aug 2011
9	CalRes 2109	TBA	Perchlorate	July 2009	Sept 2011
	PWA2	TBA	Perchlorate	Jan 2008/April 2011	
10	SIR-100	TEA	Perchlorate	July 2005	Sept 2011

The majority of the plants sampled use anion exchange to remove either nitrate or perchlorate, while Site 1 uses anion exchange to remove natural organic matter (NOM). Two of the sites employ TMA resins and two sites use the same DMEA resin, A300E. These were chosen to observe how the resin behave in different settings. Three sites use TBA resins, including two with Resin PWA2, while two sites use the same TEA resin, SIR-100, and one site uses the bi-functional TEA/TBA Resin A532E. The resins used for perchlorate removal tend to be non-regenerable resins owing to the high selectivity of the

resins for perchlorate, which makes on-site regeneration difficult. All of these resins were found to release noteworthy levels of nitrosamine precursors in previous laboratory studies (see Chapters 2 and 3).

As the treatment trains at each plant had differing configurations and operated differently, each plant is described individually along with the results.

Materials

NDMA, NDEA, NDBA, and d6-NDMA standards were obtained from Accustandard (New Haven, CT). d10-NDEA and d18-NDBA were obtained from CDN Isotopes (Pointe Claire, Quebec, Canada). EPA Method 521 method-specific activated carbon solid-phase extraction (SPE) cartridges were purchased from Restek (Bellefonte, PA). Laboratory-grade water (LGW) was prepared using a system consisting of filters, granular activated carbon adsorbers, mixed-bed ion exchange resins and UV irradiation treatment. The LGW was analyzed periodically and no nitrosamines or nitrosamine precursors were detected. All other chemicals were purchased from Fisher Scientific (Pittsburgh, PA) and were reagent-grade or higher.

Sample Collection

Grab samples of anion exchange process influent and effluent were collected in 2.5-L amber glass bottles that had rinsed with acetone and baked at 400°C to remove any nitrosamine precursors. Sample bottles were placed in styrofoam inserts, packed in coolers with blue ice, and shipped to the water plants after prior arrangements had been made as to where and when the samples should be collected. The samples were returned by overnight carrier to the University of North Carolina, where they were stored at 4°C

until analysis. Samples were analyzed for NDMA, NDEA and NDBA and their corresponding precursors within one week of receipt.

Continuous-flow Column Experiments

A sample of exhausted Resin A532E, a bi-functional TEA/TBA resin, was obtained from one drinking water treatment plant when the exhausted resin was being replaced with fresh resin. A sample of the fresh Resin A532E being installed was also obtained, and the two resins were subjected to identical continuous-flow column experiments similar to those described previously (see Chapter 3). Two hundred mLs of the resin were packed into glass chromatographic columns with an inner diameter of 2.5 cm. LGW containing 10 mM phosphate buffer at pH 7 was passed through the columns at a flow rate of 66.7 mL/min, resulting in an empty bed contact time (EBCT) of 3 min. This EBCT is typical of contact times used for ion exchange in water treatment practice. After 100 bed volumes (BV) of flow, the resins were regenerated with 600 mL (3 BV) of a 10% NaCl solution. Samples (2.0 L, 10 BV) were collected at the beginning of the column experiments, after 40 BV of flow, and immediately before and after regeneration, and analyzed for nitrosamines and nitrosamine precursors.

Nitrosamine Analysis

Samples for nitrosamine analysis (1.0 L) were spiked with 50 ng/L d6-NDMA, d10-NDEA and d18-NDBA for quantitation by isotope dilution, and extracted using activated carbon SPE cartridges. The cartridges were eluted with 30 mL of methylene chloride. LGW (1-2 mL) was added to the extracts and the methylene chloride was removed using a rotary evaporator. The extracts were analyzed by ultra-performance liquid chromatography (UPLC) tandem mass spectrometry in the positive electrospray

ionization mode using a Waters Acquity UPLC BEH phenyl column (100 mm x 2.1 mm x 1.7 µm). The mobile phase consisted of a 0.2 mM aqueous formic acid solution and methanol. The percentage of methanol in the mobile phase began at 10% and increased from 10% to 45% from 0 to 4 min and from 45% to 95% from 4 to 6 min, remained at 95% from 6 to 9 min, then decreased from 95% to 10% from 9 to 10 min, remaining at 10% for a 2 min re-equilibration period. Analyte identity confirmation was achieved by comparing retention times and product ion ratios of sample analytes with those of standards. Multiple reaction monitoring details are presented in Table 4.2.

Table 4.2. Precursor and product ions for nitrosamine analysis.

Nitrosamine	Precursor Ion	Product Ions	Product Ion Ratio	Collision Voltage
NDMA	75	43/58	0.31	17
d6-NDMA	81	46/64	0.33	17
NDEA	103	75/47	0.056	28
d10-NDEA	113	81	0.90	12
NDBA	159	103/57	0.12	28
d18-NDBA	177	113/66	0.50	10

Average method recoveries of analytes in LGW were 80.1% for NDMA, 74.8% for NDEA, and 68.0% for NDBA. Matrix effects in treatment plant water samples were corrected for using isotope dilution with a deuterium-labeled surrogate for each analyte. The limits of quantitation (LOQ), defined as the nitrosamine concentrations that resulted in responses with signal to noise ratios greater than 10, were 4.9 ng/L for NDMA, 1.4 ng/L for NDEA and 1.3 ng/L for NDBA.

Nitrosamine Formation Potential Analysis

Samples (1.0 L or 500 mL) were buffered at pH 6.8 with 20 mM phosphate and dosed with excess preformed monochloramine (140 mg/L NH_2Cl as Cl_2) in accordance with the method described by Mitch et al. (2003). After a 10-day reaction time, samples were quenched with ascorbic acid and analyzed for nitrosamines. The nitrosamine formation potential (NFP) was calculated by subtracting the corresponding ambient nitrosamine values from those formed by chloramination This NFP analysis is intended to quantify nitrosamine precursors released from the resins.

Results

Site 1

Site 1 employs Resin A300E, a DMEA resin, for the removal of nitrate. Resin vessels have a bed volume of 314 cubic feet and are operated at a flow rate of 420 gallons per minute, giving an EBCT of 5.6 minutes. Resins are regenerated with NaCl after 700,000 gallons of water have been treated, approximately every 28 hours. The resin was installed in March 2001 and samples were collected in April 2011 and August 2011.

Samples of the influent and effluent of one anion exchange vessel were taken: 1) immediately before the vessel was taken offline for regeneration, 2) immediately after the vessel was placed back online after regeneration and rinsing, 3)1 hour (10.7 BV) after the vessel was placed back online, and 4) 14 hours (150 BV) after the vessel was placed back online, or halfway through the operating cycle, between regenerations. None of the influent samples were found to contain quantifiable levels of nitrosamines or nitrosamine precursors. The results for each effluent sample are shown in Figure 4.1. Elevated levels

of nitrosamines and nitrosamine precursors were observed in each effluent sample collected at Site 1. As anion exchange influent samples did not contain nitrosamines or precursors, it is evident that contamination was a result of anion exchange treatment with Resin A300E. The spikes in nitrosamines immediately after regeneration and in nitrosamine precursors 1 hour after regeneration support the previously reported bench-scale findings that regeneration can cause increased contamination (see Chapter 3). In the earlier laboratory studies, only nitrosamine formation potential increased and the increase was immediate. In these field observations at Site 1, both NDMA and NDMA precursors increased after regeneration, and there was a delay in the increase in precursor release.

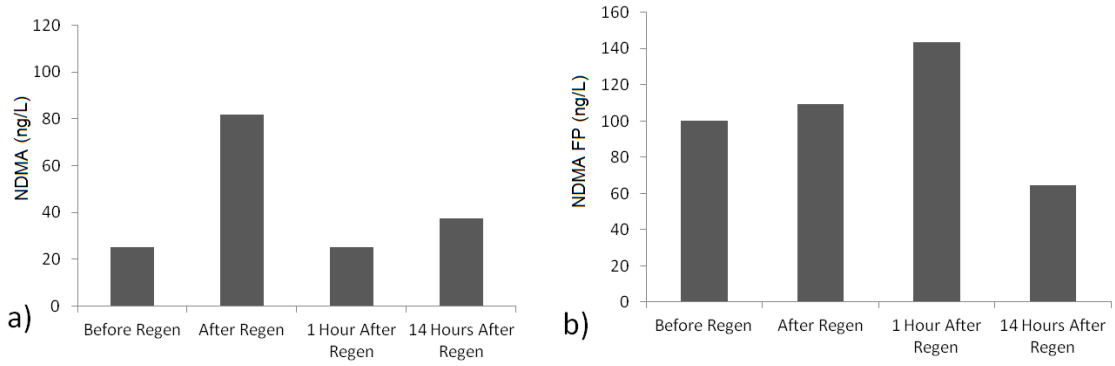


Figure 4.1. NDMA in Site 1 effluent samples. a) NDMA; b) NDMA formation potential.

A second round of sampling conducted at this site 5 months later did not confirm these results. The influent sample collected 1 hour after regeneration contained 112 ng/L NDMA, while none of the other samples contained NDMA. NDMA precursors (8.4 – 58.5 ng/L) were detected in all influent and effluent samples collected.

In the California Department of Health Services study (CAHS, 2002), two rounds of sampling were conducted. Samples of effluents from 4 plants had NDMA

concentrations that differed by at least 10 ng/L between the two sampling rounds, with one plant's NDMA concentration changing by 62 ng/L. This indicates that nitrosamine concentrations at the same plant can be highly variable between sampling times, as observed at Site 1.

Site 2

Because Resin A300E was observed to release NDMA and NDMA precursors during treatment at Site 1, another site using A300E was sought out for sampling. Site 2 uses four vessels of Resin A300E in parallel for nitrate removal. Vessels have a BV of 392 cubic feet and operate at a flow rate of 275 gallons per minute, for an EBCT of 10.7 minutes. Resins are regenerated with NaCl every 27.7 hours, or 155 BV. The resin was installed in February 2006 and samples were collected in July 2011.

Samples of the influent and effluent of one anion exchange vessel were taken: 1) immediately before the vessel was taken offline for regeneration, 2) immediately after the vessel was placed back online after regeneration and rinsing, and 3) midway through the regeneration cycle. None of the effluent samples contained quantifiable levels of nitrosamines. Influent samples contained 15-20 ng/L of NDMA precursors while effluent samples did not contain quantifiable levels of any precursors.

Site 3

Site 3 employs two vessels of CalRes 2109, a TBA resin, for perchlorate removal. The beds each have a BV of 424 cubic feet and are operated in series at a flow rate of 700 – 2000 gallons per minute for an EBCT of 1.6 - 3.5 minutes. The resins are intended for single-use and are not regenerated. The resin in the lead vessel was installed in November, 2009 and the resin in the lag vessel was installed in July, 2010. Samples were

collected in July 2011. The resins at this plant are regularly taken offline for periods of several months at a time due to groundwater availability issues – recently, they were offline from March to July of 2010, from December 2010 to February 2011, and again from April to July of 2011.

Samples of the water that had been standing in each vessel during this most recent period of downtime were collected. Additionally, influent and effluent samples were collected from each vessel 1 hour after flow had resumed. The water that had been standing in the lead vessel contained 7.9 ng/L NDMA, 75.2 ng/L NDBA and 15.4 ng/L of NDMA precursors. The water that had been standing in the lag vessel contained 61.2 ng/L NDBA and 7.9 ng/L of NDMA precursors. One hour after flow resumed, anion exchange influent contained 6.4 ng/L NDBA while the lead vessel effluent contained 43.5 ng/L NDBA and the lag vessel effluent contained 46.7 ng/L NDBA. It is likely that, with continued operation, residual NDBA would have been washed away. These elevated nitrosamine levels support the previously reported bench-scale findings that prolonged contact of resins with water can cause increased contamination (see Chapter 3). The bench-scale experiments had shown that nitrosamine precursor levels rose with prolonged contact between resins and water, while these field observations also indicate a rise in the actual nitrosamine itself. This was also noted in the observations from Site 1.

Site 4

Site 4 employs two treatment trains consisting of Resin A520E, a TEA resin, for the removal of nitrate in series with Resin A532E, a bi-functional TEA/TBA resin, for the removal of perchlorate. The A532E beds precede the A520E beds. Each train has multiple beds of A520E and A532E operating in parallel. The A520E vessels have BVs

of 25 cubic feet and are operated at an average flow rate of 57.6 gallons per minute for an EBCT of 3.2 minutes, and are regenerated with a 26% sodium chloride brine solution every 600 BV of flow. The A532E vessels have BVs of 1000 cubic feet and are operated at an average flow rate of 750 gallons per minute for an EBCT of 10 minutes. Fresh Resin A520E was installed in Train A in March 2010 and in Train B in January 2005. Fresh Resin A532E was installed in Train A in December 2010 and in Train B in January 2011. Samples were collected in August 2011.

Influent samples taken from Train A and Train B contained no detectable nitrosamines or precursors. Samples taken of Resin A532E effluent from one of the vessels in Train A and one of the vessels in Train B contained no detectable nitrosamines or precursors. Two samples of Resin A520E effluent were taken from Train A, one from a bed that was soon to be regenerated (at the end of a cycle) and one that recently had been regenerated (at the beginning of a cycle). Three samples of Resin A520E effluent were taken from Train B; one from a vessel soon to be regenerated, one from a vessel that had been recently regenerated, and one from a vessel midway through the regeneration cycle. The Train A sample taken at the end of the cycle contained 31.9 ng/L NDMA, 114 ng/L of NDMA precursors and 20.4 ng/L of NDEA precursors. The analogous Train B sample contained 31.6 ng/L NDMA and 8.3 ng/L of NDMA precursors. The Train B sample taken from a vessel midway through the cycle contained 15 ng/L of NDMA precursors and 3.4 ng/L NDEA precursors.

Site 5

Site 5 uses A530E, a TEA resin, to remove nitrate. Vessels with a 233 cubic foot BV are operated at a flow rate of 500–800 gallons per minute for an EBCT of 2.2-3.5

minutes. The resins are regenerated with NaCl after 1.5 million gallons (861 BV) of water have been treated. The resin was installed in 2001 and samples were collected in June 2011.

Influent and effluent samples of one anion exchange vessel were taken: 1) immediately before the vessel was taken offline for regeneration, 2) immediately after the vessel was placed back online after regeneration and rinsing, 3)1 hour (approximately 20 BV) after the vessel was placed back online, and 4) halfway through the operating cycle. Influent and effluent samples contained 5-9 ng/L of NDMA precursors throughout the course of sampling. Only one sample contained quantifiable levels of nitrosamines; the effluent sample collected 1 hour after regeneration contained 15.8 ng/L NDMA. No NDEA or NDEA precursors were detected.

Site 6

Site 6 uses Resin PWA2, a TBA resin, for perchlorate removal and Resin SIR-100, a TEA resin, for nitrate removal. Each of the resin vessels has a BV of 24.7 cubic feet, and the PWA2 vessels are operated at a flow rate of 45 gallons per minute for an EBCT of 4.1 minutes, while the SIR-100 vessels are operated at a flow rate of 50 gallons per minute for an EBCT of 3.7 minutes. The treatment train consists of 20 PWA2 vessels in parallel followed in series by 18 SIR-100 vessels in parallel.

Effluent samples were collected from PWA2 Vessel A (Age: 42,229 BV) and PWA2 Vessel B (Age: 104,354 BV), along with the corresponding influent to the PWA2 vessels. Likewise, influent to the SIR-100 vessels was sampled, and corresponding samples were collected from SIR-100 Vessel A (444 BV after regeneration, soon to be regenerated again), SIR-100 Vessel B (22.9 BV, or 1 hour after regeneration) and SIR-

100 Vessel C (225.9 BV after regeneration, or midway through a cycle). The sample of PWA2 influent contained 1.3 ng/L of NDBA precursors, while the effluent from Vessels A and B contained 1.7 ng/L and 7.6 ng/L of NDBA precursors, respectively. SIR-100 influent contained no quantifiable nitrosamines or precursors, while the effluent from SIR-100 Vessel B, the sample taken 1 hour after regeneration, contained 7.2 ng/L of NDBA precursors.

Site 7

Site 7 uses Resin A860, a TMA resin, for removal of natural organic matter. The resin has a 400 cubic foot BV and is operated at a flow rate of 950 gallons per minute, for an EBCT of 3.5 min. The resin is regenerated with NaCl every 11.9 hours, or 204 BV. The resin was installed in April 2009 and samples were collected in March 2011 and August 2011.

Samples of the influent and effluent of one anion exchange vessel were taken: 1) immediately before the vessel was taken offline for regeneration, 2) immediately after the vessel was placed back online after regeneration and rinsing, 3)1 hour (17 BV) after the vessel was placed back online, and 4) 4 hours (68 BV) after the vessel was placed back online. No quantifiable levels of nitrosamines were detected in any of the samples. Influent and effluent samples collected in March 2011 contained 58-104 ng/L of NDMA precursors at each sampling time, with influent and effluent samples having comparable levels. A sample of anion exchange influent collected 5 months later was not found to contain any NDMA precursors.

Site 8

Site 8 uses eight parallel vessels of IRA910, a TMA resin, for nitrate removal. Each vessel has a 450 cubic foot BV and is operated at a flow rate of 100 gallons per minute, for an EBCT of 3.4 minutes. Resins are regenerated every 24 hours (424 BV). The resins were installed in 1992 and samples were taken in September 2011. The ion exchange system operates seasonally, as needed.

At the time of sampling, the ion exchange system had been offline for several months. Prior to sampling, the resins were brought back into service and went through three full regeneration cycles. Influent and effluent samples were taken from Bed A: 1) immediately before the third regeneration, 2) immediately after regeneration and rinsing, 3) 1 hour after the bed was brought back online after regeneration, and 4) 12 hours (212 BV) after regeneration, or midway through a typical operating cycle. Effluent samples were also taken from Beds B and C immediately before and after the third regeneration. None of the samples collected at this site contained quantifiable levels of nitrosamines or nitrosamine precursors despite the findings from earlier laboratory studies (see Chapters 2 and 3) that this resin had the highest release of NDMA precursors, especially after flow interruption.

Site 9

Site 9 uses Resins PWA2 and CalRes 2109, both TBA resins, for perchlorate removal. The PWA2 configuration consists of two treatment trains in parallel, each consisting of two vessels in series. The vessels each have a BV of 300 cubic feet and are operated at a flow rate of 1500 gallons per minute for an EBCT of 1.5 min. The resin in Train A was installed in April 2011 and the resin in Train B was installed in January 2008. The CalRes 2109 treatment configuration consists of two vessels in parallel

followed in series by another two vessels in parallel. The vessels each have a BV of 425 cubic feet and are operated at a flow rate of 2000 gallons per minute for an EBCT of 1.6 min. The resins in the CalRes 2109 vessels were installed in July 2009. Samples were collected in August 2011. None of the resins are regenerated, and the vessels are estimated to be in use 60% of the time.

Samples of the influent and final effluent of the CalRes 2109 process train were collected. Influent, lead vessel effluent and lag vessel effluent samples were collected from each PWA2 train. No sample contained quantifiable levels of nitrosamines or nitrosamine precursors.

Site 10

Site 10 uses Resin SIR-100, a TEA resin, for perchlorate removal. The resins are intended for single-use and are not regenerated. There are 16 SIR-100 vessels operated in parallel, with 10 vessels online at any one time. The vessels each have a BV of 24.7 cubic feet and are operated at a flow rate of 74.8 gallons per minute for an EBCT of 2.47 minutes. Several days prior to sampling, the ion exchange beds were cleaned and disinfected by the utility using free chlorine to control microbial growth that had developed in the system. The utility collected samples and analyzed for nitrosamines after disinfection at the direction of the California Department of Public Health and found that nitrosamine levels were below regulatory limits, but did not analyze for nitrosamine precursors. Samples were collected in September 2011.

Anion exchange influent and the effluents of three different vessels were sampled. Vessel A had a resin age of 13,738 BV, Vessel B had a resin age of 22,339 BV and

Vessel C had a resin age of 51,499 BV at the time of sample collection. None of the samples collected contained quantifiable levels of nitrosamines or nitrosamine precursors.

Column experiments with fresh and exhausted resins

The releases of nitrosamine precursors by each of the A532E resins during the bench-scale continuous-flow column experiments are presented in Figure 4.2. One of the columns contained spent resin that had been used in a drinking water treatment plant for perchlorate removal for 29 months. The other column contained fresh sample of the same resin.

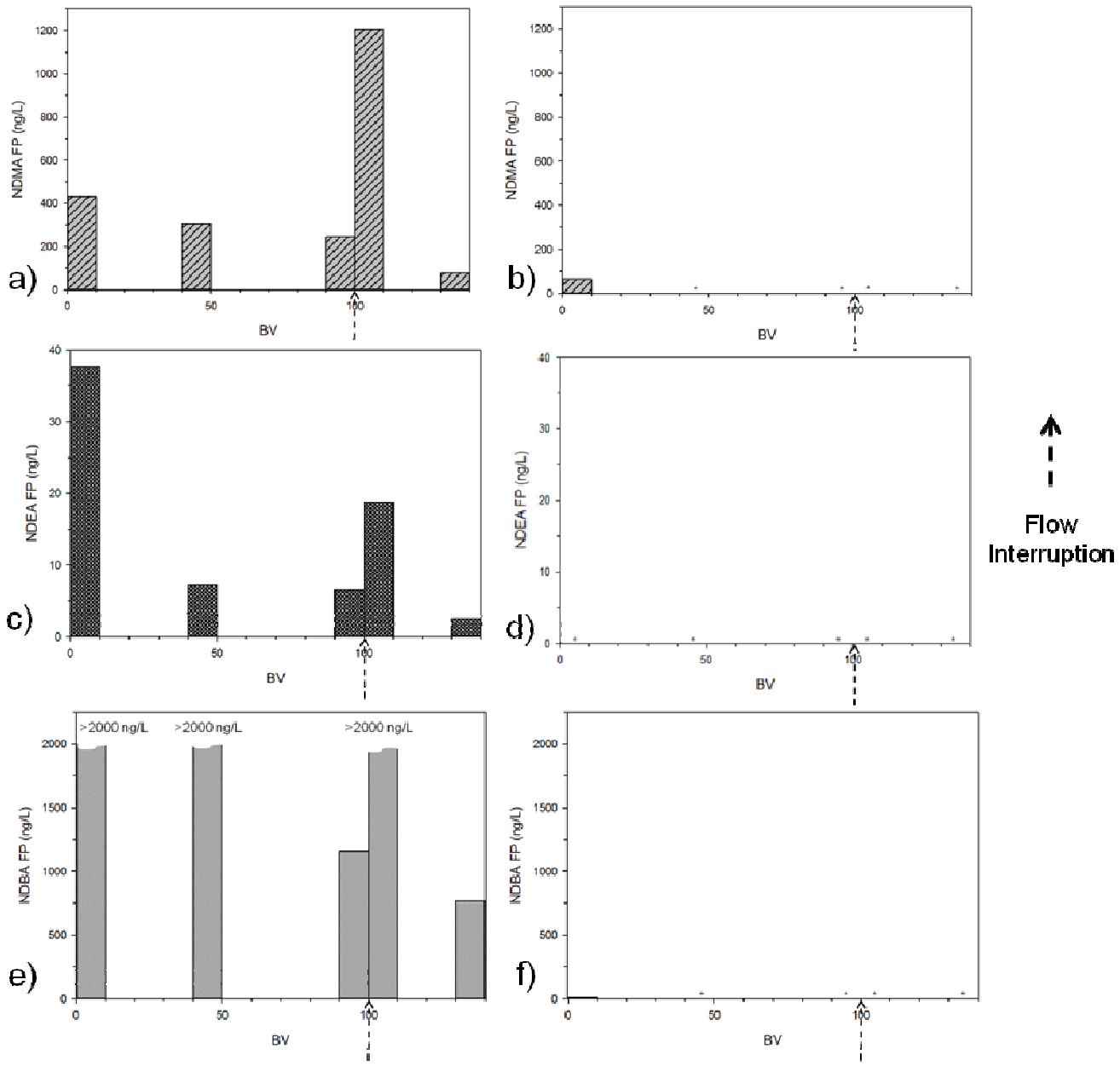


Figure 4.2. Release of nitrosamine precursors by fresh and spent A532E during column experiments. a) NDMA precursors from fresh resin; b) NDMA precursors from spent A532E; c) NDEA precursors from fresh resin; d)NDEA precursors from spent resin; e) NDBA precursors from fresh resin; f) NDBA precursors from spent A532E. (* Indicates that a sample was taken and nitrosamines were below the LOQ.)

The fresh resin released high concentrations of NDMA, NDEA and NDBA precursors throughout the experiments, including high levels in the first 10 BV (432 ng/L

NDMA, 38 ng/L NDEA and >2000 ng/L NDBA precursors), and appreciable increases after a 12-14-hour flow interruption. In contrast, the spent resin released NDMA and NDBA precursors at levels much lower than the fresh resin and did not release detectable NDEA precursors. Flow interruptions, which have been shown to result in increased precursor releases even in resins with low releases during the first 10 BV of flow (see Chapter 3), did not result in an increase in nitrosamine precursor release for the spent resin. With respect to actual nitrosamine release, the only release by the fresh A532E was an NDMA release of 115 ng/L in the first 10 BV of flow (not shown). This is consistent with previous laboratory findings for this resin (see Chapter 3). The spent A532E released low (<5 ng/L) levels of NDBA throughout the column experiment, with a jump to 7.7 ng/L NDBA after a 12-14-hour flow interruption.

Full-scale influent and effluent samples could not be collected from the plant where Resin A532E was being used for treatment.

Discussion

From an analytical standpoint, the dual confirmation of analytes through chromatographic retention time and multiple reaction monitoring ensured proper identification of the analytes measured in this field study. Nitrosamines were quantified by isotope dilution using a specific deuterium-labeled standard for each analyte in order to correct for matrix effects, so the concentrations given above can be considered reliable. Replicate samples were collected and analyzed for several plants. These samples showed consistent findings in that they all had nitrosamine and nitrosamine precursor levels below quantitation limits, but a statistical analysis of reproducibility was not possible.

Nitrosamine precursors were found in the anion exchange influent samples collected at five of the sites (Sites 1, 2, 5, 6 and 7). The majority of NDMA precursors in natural waters have unidentified structures (Padye et al., 2009) and are thought to be present in the high-nitrogen fractions of NOM (Dotson et al., 2009). Many of the sites sampled use groundwater as a raw water source. While groundwaters typically have low DON concentrations (Westerhoff and Mash, 2002), NOM in some groundwaters is nitrogen-rich, with low DOC/DON ratios (Thurman and Malcolm, 1981). Site 3 contained 6.4 ng/L NDBA in the anion exchange influent. While NDBA has recently been detected in raw drinking waters at concentrations as high as 19.9 ng/L (Wang et al., 2011), it has not previously been reported in drinking water treatment plants using groundwater as a source.

Anion exchange influent samples collected at Site 2 contained noticeable NDMA precursor levels (14.9 – 20.3 ng/L), but anion exchange effluent samples did not contain any NDMA precursors. NOM, a known precursor of NDMA (Dotson et al., 2009), contains negatively charged functional groups at water treatment pH levels and can be effectively removed by anion exchange resins (e.g. Bolto et al., 2002). It is likely that the NDMA precursors in the anion exchange influent at Site 2 were incorporated within NOM macromolecules and were removed through the anion exchange process.

Analysis of the findings indicates that resins may be a greater source of nitrosamine contamination earlier in their treatment lives, and that resins which have been in place for long periods of time are not likely to exhibit nitrosamine or nitrosamine precursor levels of concern. The different observations at plants using Resin A520E illustrate this point. At Site 4, the Resin A520E effluent sample taken from Train A

contained appreciably higher levels of NDMA and precursors of NDMA and NDEA than did the samples taken from Train B, where the resin had been in service five years longer than the resin in Train A.

The observations at Site 8 also seem to support this conclusion. Resin IRA400, a TMA resin, was shown in previous bench-scale research (see Chapters 2 and 3) to be one of the resins releasing the greatest amounts of nitrosamines and nitrosamine precursors from among a large number of resins examined. The observation that all of the samples collected from IRA400 effluent at Site 8 were free of nitrosamines and nitrosamine precursors is most likely due to the fact that the resin was installed in 1992, a full 19 years before sampling, and that any residual tri- or dialklyamine compounds remaining from resin synthesis had been fully washed away before sampling occurred.

Finally, column experiments performed with fresh and exhausted Resin A532E clearly demonstrated that, while the fresh resin released appreciable nitrosamines and nitrosamine precursors, the exhausted resin no longer released these contaminants. It is likely that nitrosamines and precursors were present in the exhausted resin when it was newly installed and were washed away during 29 months of use in treatment.

Conclusions

Out of ten drinking water treatment plants surveyed that use anion exchange for the removal of nitrate, perchlorate, arsenic, and NOM among other anionic contaminants, three plants contained noteworthy levels of nitrosamines in their ion exchange effluents. It should be noted that all three of these plants contained nitrosamine concentrations above 10 ng/L, a likely level of regulatory concern. A greater percentage (five out of ten) had noteworthy levels of nitrosamine precursors in their ion exchange effluents. [It must

be noted that the nitrosamine precursor measurements reported in this study reflect the nitrosamine formation potential and are not an indication of the actual levels that will be formed for typical distribution system practices because of the high levels of preformed monochloramine used in the formation potential analysis. Nevertheless, the fact that these precursors are found in the ion exchange effluent suggests that nitrosamines can be formed at undesirable levels when finished water is chloraminated.

The effects of resin regeneration and resin downtime on nitrosamine and nitrosamine precursor release reported earlier in laboratory studies (see Chapter 3) were each illustrated to some degree by the results obtained at full-scale treatment facilities. Appreciable concentrations of nitrosamine precursors were detected in the anion exchange influents at several sites, and anion exchange treatment actually removed nitrosamine precursors in one instance. The results suggest that, as resins are used in treatment, their nitrosamine and nitrosamine precursor contribution diminishes.

In this study, one-time grab samples were collected from plants employing anion exchange treatment. The observations reported suggest that nitrosamine and nitrosamine precursor levels will be different at each plant using this technology, and that utilities should be attentive to the potential for high levels of nitrosamines and their precursors, especially when new resins are installed, after regeneration, and after extended periods of downtime. More research is needed to fully determine the extent and the persistence of nitrosamine contamination at anion exchange plants and to develop a treatment protocol that can effectively minimize the addition of nitrosamines and nitrosamine precursors to water treated by anion exchange resins.

Chapter 5. Conclusions and Recommendations for Future Research

Conclusions

The release of nitrosamines by some resins and the release of nitrosamine precursors by many resins among a large group of anion exchange resins used in water treatment practice was demonstrated and confirmed in batch contact experiments. The release of NDEA and NDEA precursors by TEA resins in a drinking water treatment context and the release of NDPA by a TPA resin were reported here for the first time. The release of three nitrosamines by one bi-functional resin (A532E) and the release of NDMA precursors by resins manufactured with TEA and TBA functional groups were demonstrated and highlighted. The importance of resin cleaning and the consequent inability of batch contact studies to definitively address nitrosamine release were noted, and continuous-flow column studies that allow for the monitoring of nitrosamine and nitrosamine precursor levels as resins are rinsed were recommended and undertaken.

In continuous-flow column studies, anion exchange resins were found to release elevated levels of nitrosamines and nitrosamine precursors at the start of experiments designed to simulate operations in full-scale drinking water treatment plants. Nitrosamine concentrations typically fell below levels of regulatory concern within 100 BV of throughput, while nitrosamine formation potential generally stayed above 10 ng/L throughout the column experiments. Regeneration of the resins with NaCl, as practiced in treatment plants, led to noticeable increases in nitrosamine precursor concentrations. The

elevated levels decreased quickly with continued column flow. Changes in resin swelling due to the change in resin ionic form and the ionic strength of the regenerant solution during regeneration were proposed as the causes of the nitrosamine precursor spikes. Flow interruptions of 12-14 hours resulted in nitrosamine precursor spikes typically larger than those due to regeneration. These increased precursor concentrations also decreased quickly with column flow. The increased concentrations are likely due to water penetrating resin polymer structures more deeply during prolonged contact time and allowing deeply embedded precursors to enter the aqueous phase and be released when flow resumes.

Residual trialkylamines present as unreacted materials from resin synthesis are proposed as the source of the nitrosamine precursors observed. In the cases of NDMA precursor release by resins manufactured with TEA or TBA functional groups, the NDMA precursors are believed to be TMA present as impurities in TEA or TBA starting materials. A large amount of these precursors are rinsed from the resins at the beginning of flow, and precursors that are more deeply embedded in the polymer structures are released during changes in resin swelling and are leached out during long contact times.

Some resins were found to react with monochloramine and free chlorine in column feed water to produce nitrosamines. The quaternary amine functional groups of these resins do not offer any plausible opportunity for reaction with oxidants. It is possible, however, that DMA present as impurities in TMA used for resin synthesis became incorporated into the chemical structures of the resins. A reaction mechanism based on the attack of DMA groups by monochloramine or free chlorine resulting in the

liberation of DMA was proposed. This DMA can then react with chloramines in the feed water to form NDMA, accounting for the observed NDMA concentrations.

Out of ten full-scale drinking water treatment plants surveyed that use anion exchange, three plants contained noteworthy levels of nitrosamines in anion exchange effluent samples and five contained nitrosamine precursors in anion exchange effluent samples. This was the first study to include NDEA and NDBA analysis in a field survey isolating anion exchange treatment. The presence of NDBA and the presence of NDEA and NDBA precursors in drinking water treatment plants as a result of anion exchange is report here for the first time.

The laboratory findings of the effects of resin regeneration and prolonged resin downtime were verified in the field by samples collected at full-scale operating anion exchange treatment plants. Many anion exchange influent samples were found to contain nitrosamines or nitrosamine precursors, possibly due to the presence of amines as constituents of NOM. In one plant, the anion exchange process was found to remove NDMA precursors. This may be due to the removal of negatively charged NOM molecules containing DMA functional groups through anion exchange.

In several cases, a plant using a given resin had nitrosamines or precursors in its anion exchange effluent while another plant using the same resin did not. In these cases, the plants without nitrosamines or precursors had been using the resins for longer periods of time than the plants with nitrosamines or precursors, suggesting that resins may be washed clean of any possible contamination with extended use. This effect was also observed in controlled bench-scale column contact studies performed with a fresh resin and a resin that had been exhausted after years of use at a full-scale treatment plant.

Previous full-scale sampling investigations of nitrosamines have included anion exchange plants among larger groups of plants for sampling. One study (CA DPH, 2002) found that 1 out of 4 anion exchange plants had elevated nitrosamine levels. Another (Valentine et al., 2006) found elevated nitrosamines in one anion exchange plant but not in another. The findings of this expanded study (3 out of 10 plants with elevated nitrosamines, 5 out of 10 with elevated precursors) corroborate the findings of the previous studies that, while the use of anion exchange indicates that nitrosamines may be a problem in water treatment practice, it does not follow that every treatment plant that uses anion exchange will have elevated nitrosamine levels. The potential for the occurrence of nitrosamines and nitrosamine precursors in full-scale anion exchange facilities must be evaluated on a plant-by-plant basis.

This research clearly demonstrated that strong base anion exchange resins can serve as sources of nitrosamines and nitrosamine precursors in drinking water treatment, most likely due to the presence of residual tri- and dialklyamines remaining from resin synthesis. Several anion exchange resins were found to release multiple nitrosamines and their precursors. Resin regeneration and downtime were found in laboratory experiments and field observations to be factors leading to an increase in nitrosamine contamination. Laboratory experiments suggested that resins can be washed clean of any residual nitrosamines and precursors, and field observations confirmed that resins that have been in place for longer periods of time tend to release lower levels of nitrosamine precursors.

An important implication of these findings is that new resins need to be rinsed or cleaned effectively before being placed into service. This may require multiple regenerations or extended rinsing. Utilities should analyze for nitrosamines and

nitrosamine formation potential before placing resin beds into service. Additionally, resin suppliers need to take care in providing contaminant-free resins for use in drinking water treatment.

Recommendations for Future Research

Laboratory Investigations

Nitrosamine precursors were found to be released by most of the anion exchange resins investigated in this study, and it was proposed that these precursors were present as unreacted trialkylamine resin synthesis materials and dialkylamine contaminants. The presence of these chemicals in resins has been tolerated to this point, but now that nitrosamines have become a public health concern, it is important to confirm that unreacted trialkylamines are in fact the source of nitrosamine precursors, and investigate ways to minimize their presence. To confirm their presence, batch or column studies similar to those performed in this study should be conducted, with waters analyzed for trialkylamines and dialkylamines. Commercial resins are prepared using technical-grade chemicals in an industrial setting; model resins could be synthesized using a more rigorous laboratory synthesis with higher purity chemicals. Batch or column leaching experiments performed with laboratory-prepared resins may yield different nitrosamine results. In fact, resins of high purity are already commercially available for pharmaceutical applications.

The presence of dialkylamines in place of trialkylamines at exchange sites was proposed as part of a mechanism for the reaction of resins with oxidants. It may be possible to detect the presence of dialkylamines in the resin structures using

spectroscopic methods such as infrared spectroscopy (IR) or nuclear magnetic resonance spectroscopy (NMR). If there are dialkylamines present, then the exchange sites with dialkylamines will function as weak base exchangers rather than as strong base exchangers and will lose their charge and therefore their exchange capacity at high pH. A measurement of the exchange capacities of resins at different pH values may give an indication of the degree to which dialkylamines are present in place of trialkylamines.

The formation of nitrosamines during the reaction of free chlorine with anion exchange resins remains unexplained. Further fundamental investigation of the different mechanisms of nitrosamine formation is required, especially as it relates to anion exchange.

The increase in nitrosamine precursor release after NaCl regeneration of resins in the laboratory studies was attributed to changes in resin swelling as resins released phosphate buffer ions in favor of chloride or to the increased ionic strength associated with regeneration. This could be further elucidated by contacting resins in columns with a feed water containing high concentrations of various anions. The resins would take up these various anions and undergo a more dramatic change in ionic form when regenerated. As the extent of resin swelling is expected to be different for each different ionic form, perhaps a more mild regeneration procedure could be developed using an anion that causes a less dramatic change in swelling than chloride, or introducing chloride in a concentration gradient, resulting in less stress on the resin.

Field Investigations

In this study, the most recently installed resin investigated in the field had been in operation for five months, while the controlled laboratory studies indicated that the

greatest nitrosamine release occurs at the beginning of column flow. It would therefore be desirable to examine resins at full-scale treatment facilities as they are installed and to collect samples at the beginning of the treatment life of a resin, including before and after the resin is regenerated for the first several times.

Various methods have been found to destroy nitrosamines, most notably UV irradiation. During this study, no plants were identified that use UV irradiation or other methods for nitrosamine destruction during drinking water treatment. It would be desirable to identify plants using these technologies and to evaluate their effectiveness in destroying nitrosamines and nitrosamine precursors. It would be particularly interesting to locate a plant that was installing fresh resin and using a nitrosamine removal technology, and to investigate the performance of the removal technology during the treatment life of the resin. Studies such as these, by definition, need to be site-specific.

Nitrosamine precursors were found in several anion exchange effluents at full-scale drinking water treatment plants. As nitrosamines are known to form during reactions between chloramines and precursors, and as chloramines are known to be persistent in the distribution system, it is important to determine the degree to which the precursors released by anion exchange resins react to form nitrosamines before reaching the consumer's tap. Samples should be taken from several locations in the distribution systems of utilities found to have nitrosamine precursors in their plant effluent and analyzed for nitrosamines to determine the actual public health risks posed by nitrosamine precursors.

Appendix A. Analytical Details

Materials

NDMA, NDEA, NDPA, NDBA, d6-NDMA and d14-NDPA standards were obtained from Accustandard (New Haven, CT) and d10-NDEA and d18-NDBA were obtained from CDN Isotopes (Pointe Claire, Quebec, Canada). EPA Method 521 method-specific activated carbon solid phase extraction (SPE) cartridges were purchased from Restek (Bellefonte, PA). Laboratory-grade water (LGW) was prepared using a system consisting of filters, granular activated carbon adsorbers, mixed-bed ion exchange resins and ultraviolet (UV) treatment. The LGW was analyzed periodically and found to contain levels of nitrosamines and nitrosamine precursors below detection limits. All other chemicals were purchased from Fisher Scientific (Pittsburgh, PA) and were reagent-grade or higher. All glassware was rendered chlorine demand-free, rinsed with acetone and baked at 400 °C for four hours. Detergent, which often contains TEA, was not used at any time during glassware preparation.

Nitrosamine Analysis

Samples for nitrosamine analysis (1.0 L) were spiked with 50 ng/L d6-NDMA, d10-NDEA, d14-NDPA and d18-NDBA for quantitation by isotope dilution and extracted using activated carbon SPE cartridges. The cartridges were preconditioned with 6 mL of methylene chloride, 6 mL of methanol, and 20 mL of LGW and eluted with 30 mL of methylene chloride. LGW (1-2 mL) was added to the extracts and the methylene chloride was removed using a rotary evaporator. The extracts were analyzed by ultra-performance liquid chromatography tandem mass spectrometry in the positive electrospray ionization mode using a Waters Acquity UPLC BEH phenyl column (100 mm x 2.1 mm x 1.7 µm). The mobile phase was composed of a 0.2 mM aqueous formic

acid solution and methanol. The percentage of methanol in the mobile phase began at 10% and increased from 10% to 45% from 0 to 4 min and from 45% to 95% from 4 to 6 min, remained at 95% from 6 to 9 min, then decreased from 95% to 10% from 9 to 10 min, remaining at 10% for a 2 min re-equilibration period. Analyte identity confirmation was achieved by comparing retention times and product ion ratios of sample analytes with those of standards. Parent and product ions and ratios are presented in Table A.1 and a representative chromatogram is shown in Figure A.1.

The limits of quantitation (LOQs) were defined as the concentrations of analytes that resulted in peaks with signal to noise ratios of 10. Representative calibration curves are shown in Figures A.2 – A.10 and LOQs are presented in Table A.2

Table A.1 Precursor and product ions for nitrosamine analysis.

Nitrosamine	Precursor Ion	Product Ions	Product Ion Ratio	Collision Voltage
NDMA	75	43/58	0.31	17
d6-NDMA	81	46/64	0.33	17
NDEA	103	75/47	0.056	28
d10-NDEA	113	81	0.90	12
NDPA	131	43/59	0.46	28
d14-NDPA	145	97/127	0.12	11
NDBA	159	103/57	0.12	28
d18-NDBA	177	113/66	0.50	10

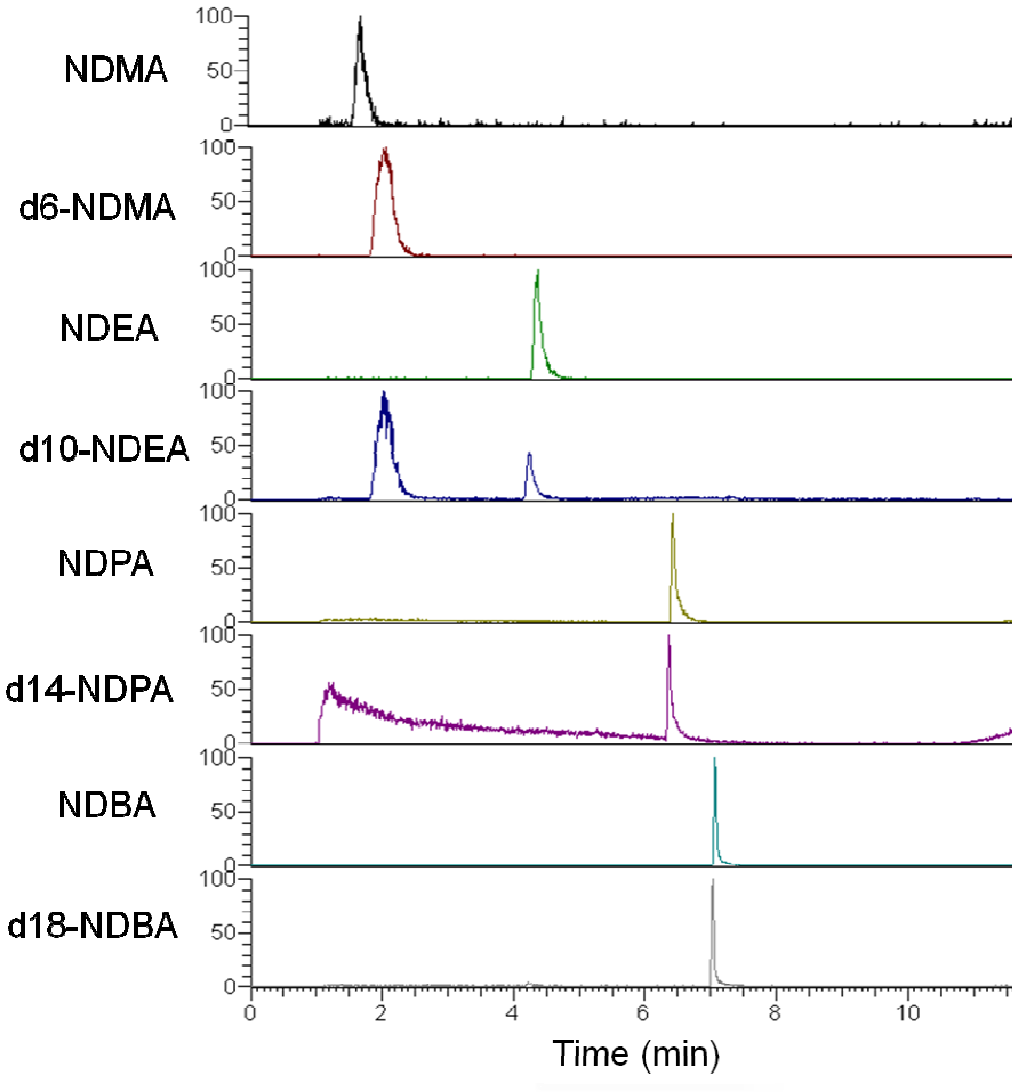


Figure A.1. Representative chromatograms of nitrosamine analytes and internal standards.

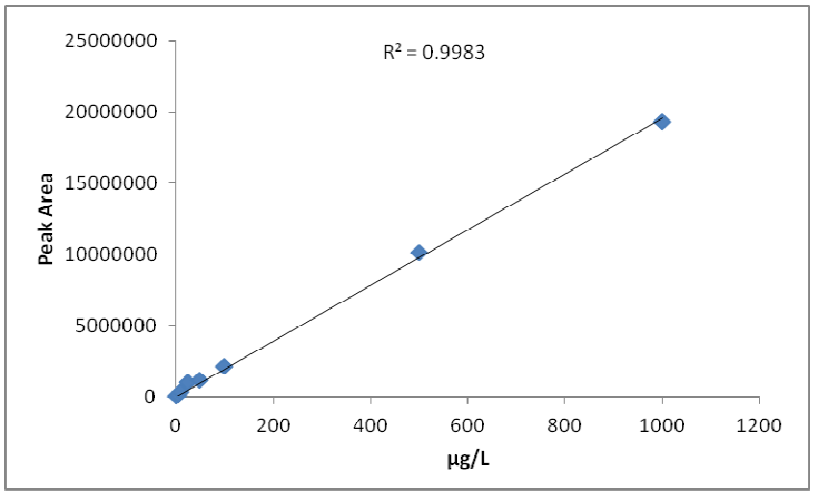


Figure A.2. Representative NDMA calibration curve.

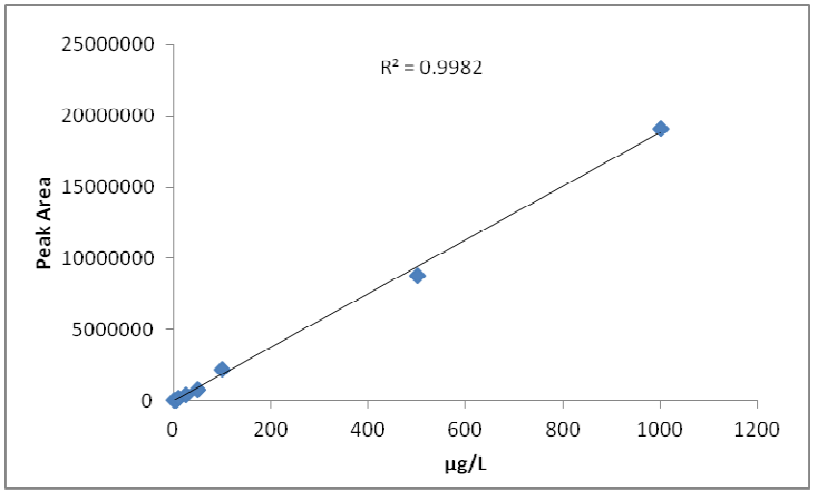


Figure A.3. Representative NDEA calibration curve.

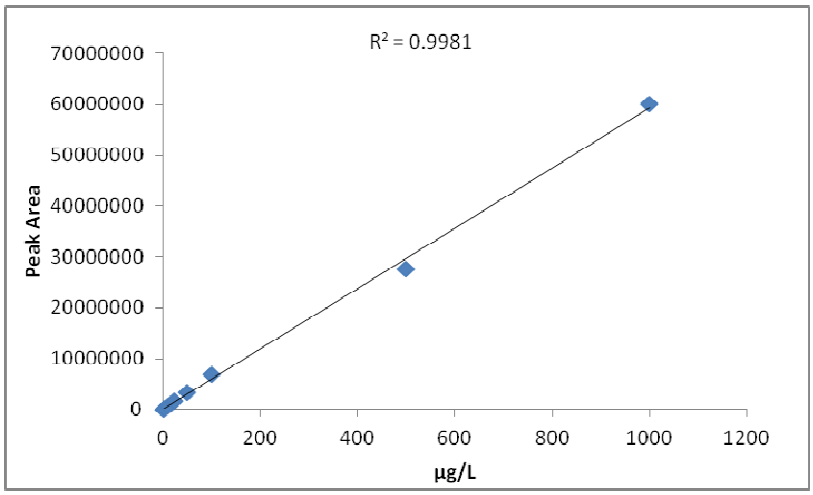


Figure A.4. Representative NDPA calibration curve.

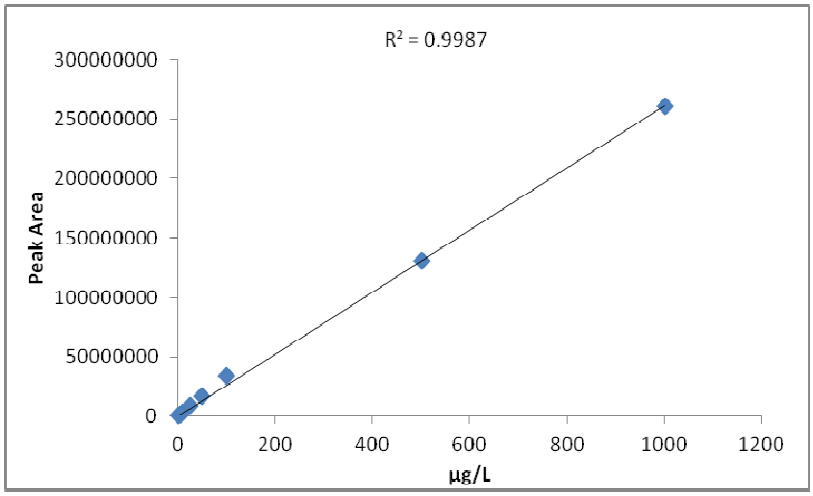


Figure A.5. Representative NDBA calibration curve.

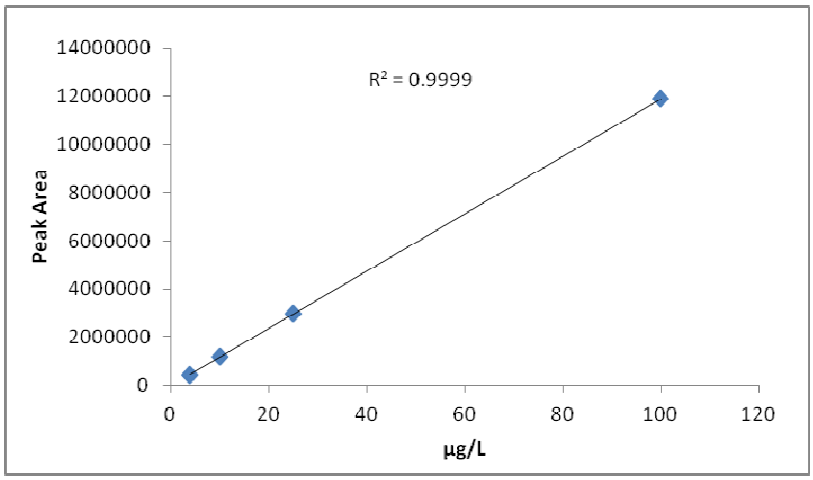


Figure A.6. Representative d6-NDMA calibration curve.

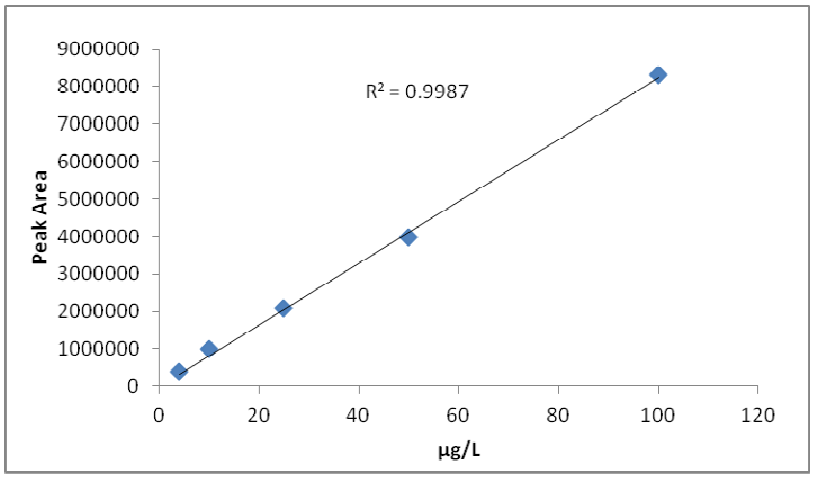


Figure A.7. Representative d10-NDEA calibration curve.

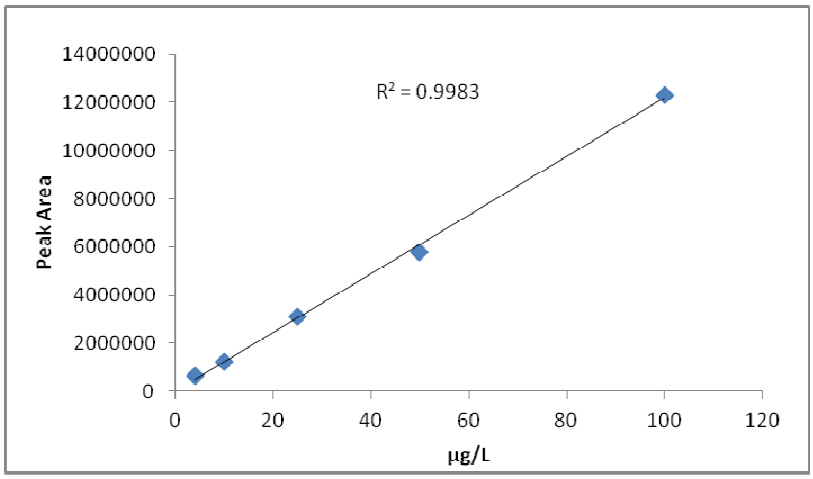


Figure A.8. Representative d14-NDPA calibration curve.

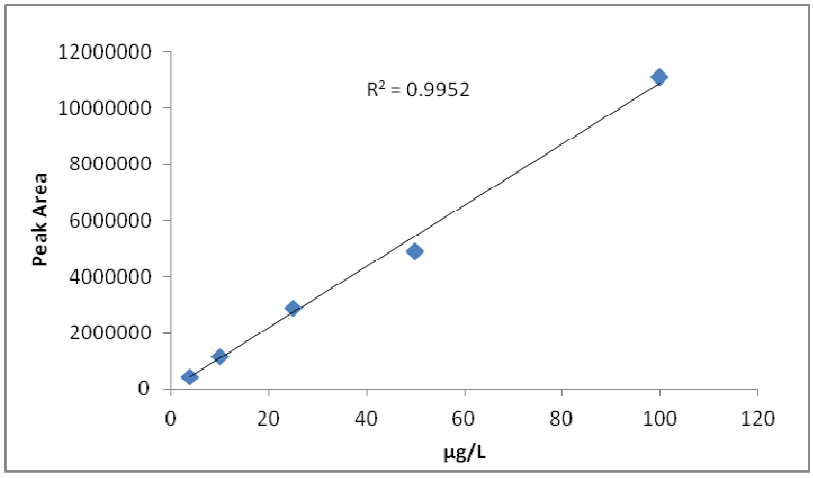


Figure A.9. Representative d18-NDBA calibration curve.

Table A.2. Analyte limits of quantitation.

Analyte	Limit of Quantitation (ng/L)
NDMA	4.9
NDEA	1.4
NDPA	3.9
NDBA	1.3

Analyte Recovery

To determine the analyte recoveries of the method, 1.0 L samples of buffered LGW with 3 mg/L ascorbic acid quenching agent added were spiked with nitrosamines at 50 ng/L and analyzed. Recoveries are listed in Table A.3.

Table A.3. Analyte recoveries.

Analyte	Recovery (%)
NDMA	80.1
NDEA	74.8
NDPA	81.2
NDBA	68.0

Appendix B. Additional Column Investigations

This appendix presents the results of additional continuous-flow column experiments referenced in Chapter 3.

Multiple Regeneration Experiments

Resins A530E and PWA5 were subjected to 10 simulated regenerations in continuous-flow column experiments. The results of these experiments are presented in Figures B.1 and B.2.

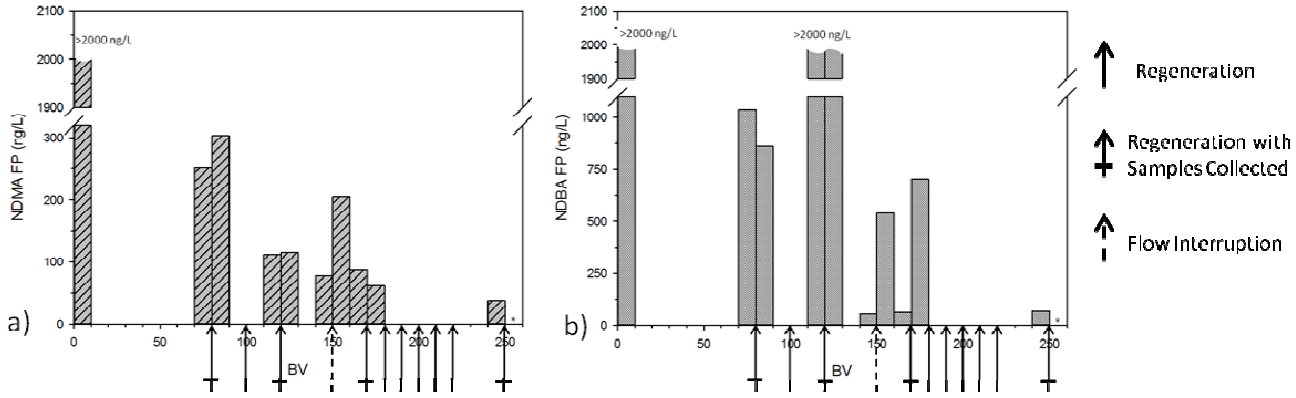


Figure B.1. Release of nitrosamine precursors by Resin A530E during multiple-regeneration column experiments. a) NDMA precursor release; b) NDBA precursor release. (* Indicates that a sample was taken and nitrosamines were below the LOQ.)

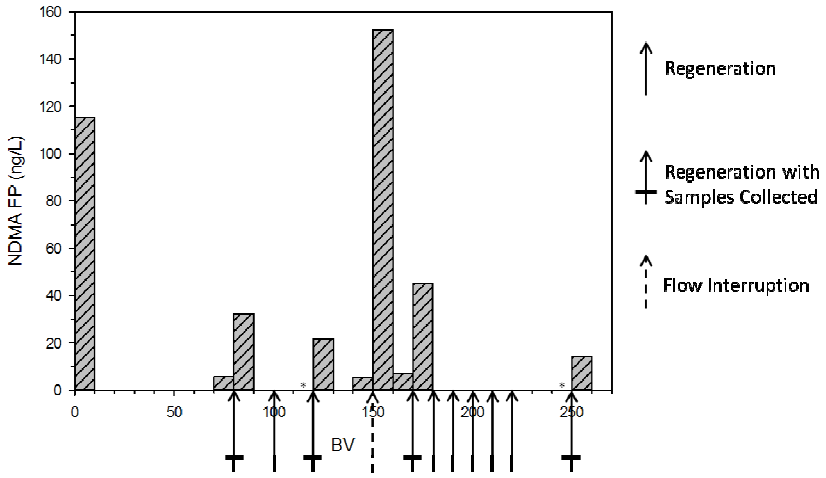


Figure B.2 Release of NDMA precursors by Resin PWA5 during multiple-regeneration column experiments. (* Indicates that a sample was taken and nitrosamines were below the LOQ.)

Resin Aging Experiments

Continuous-flow column experiments were performed upon receipt of Resins PWA5 and TAN-1 and again after the resins had been stored for 6 months at 4°C. Results from these experiments are presented in Figures B.3 and B.4.

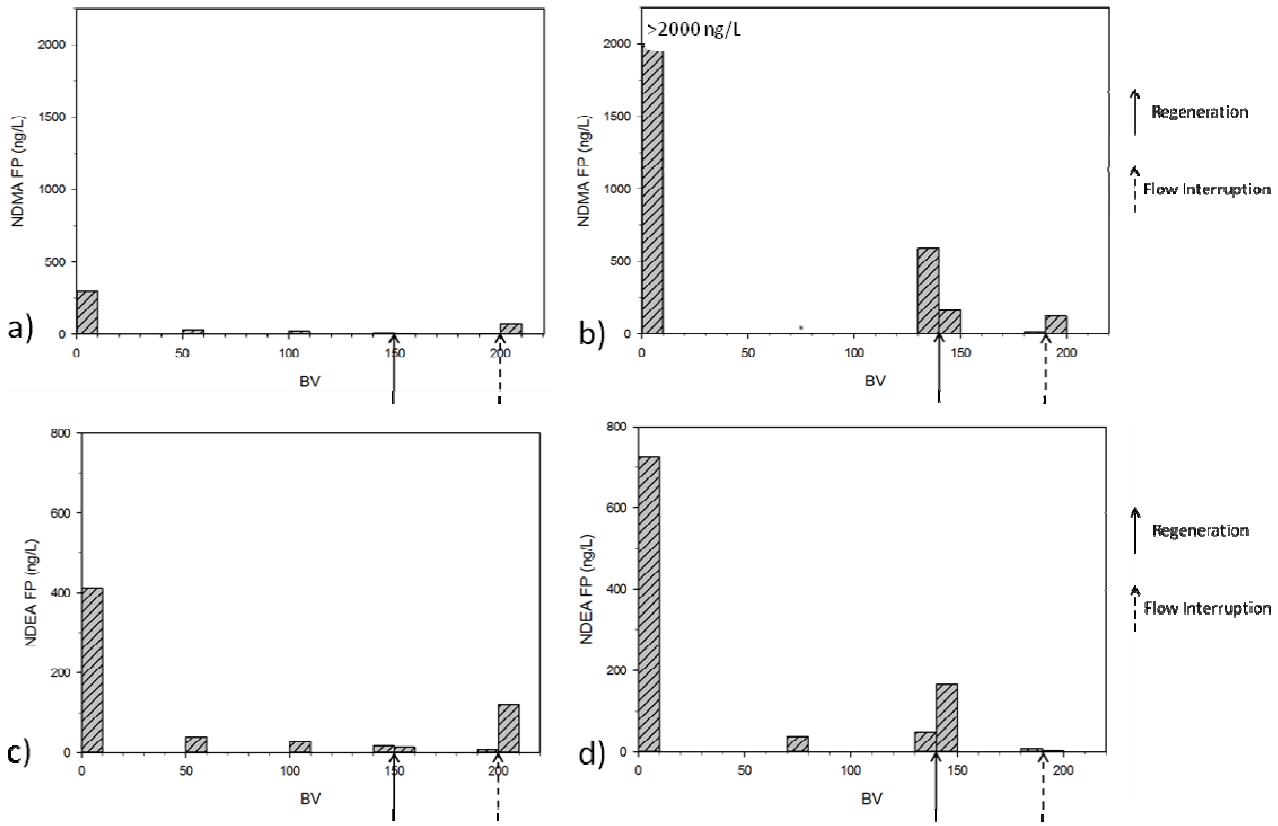


Figure B.3. Release of nitrosamine precursors by Resin PWA5 during continuous-flow column experiments. a) NDMA precursor release, t=0; b) NDMA precursor release, t=6 months; c) NDEA precursor release, t=0; d) NDEA precursor release, t=6 months. (* Indicates that a sample was taken and nitrosamines were below the LOQ.)

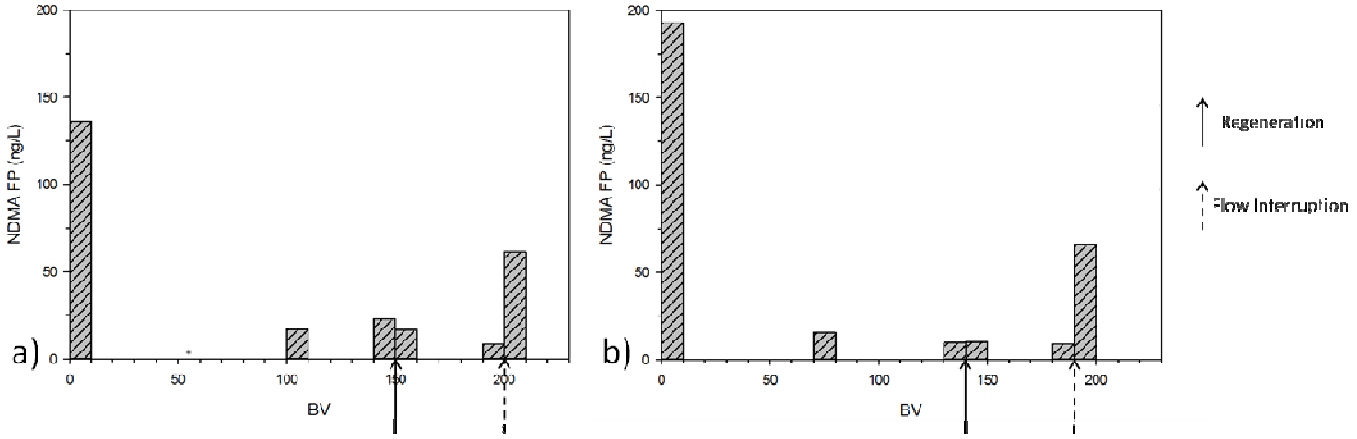


Figure B.4. Release of NDMA precursors by Resin TAN-1 during continuous-flow column experiments. a) NDMA precursor release, t=0; b) NDMA precursor release, t=6 months. (* Indicates that a sample was taken and nitrosamines were below the LOQ.)

Appendix C. Column Experiment Reproducibility

To investigate the reproducibility of the continuous-flow column experimental procedure, three identical column experiments were performed in parallel with Resin PWA15. The results of these experiments are illustrated in Figure C.1.

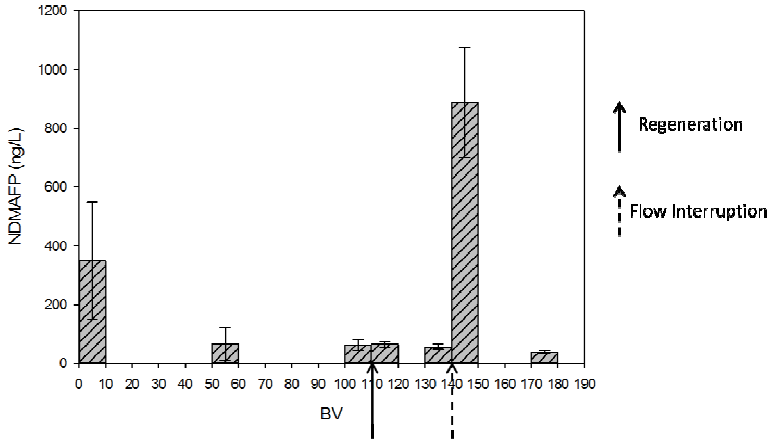


Figure C.1. Release of NDMA precursors by Resin PWA15 during 3 identical continuous-flow column experiments. Error bars represent 1 standard deviation.

None of the samples collected during these experiments contained quantifiable levels of nitrosamines themselves, although they did contain appreciable levels of nitrosamine precursors. NDMA precursor levels measured in samples collected before and after regeneration and before and after the 12-14 hour flow interruption agreed with each other within a relative standard deviation (RSD) of 30%. The initial 10 BV and the 50 BV replicate samples exhibited large standard deviations (RSD 57% and 86%, respectively), but they were reproducible in that they all showed high NDMA formation potentials. The lack of reproducibility may be due to uncertainty inherent in the process of loading the resin into the column. Resins are rinsed and contacted with water to various and unquantifiable degrees each time when the desired volume of resin is measured and placed in the column. Therefore, nitrosamine and nitrosamine precursor levels reported during the first 0-60 bed volumes of a column experiment should not be considered reliably quantitative.

Appendix D. Results of All Continuous-flow Column Contact Experiments

This appendix presents the results of the continuous-flow column studies performed for all of the resins discussed in Chapter 3. These results were used to construct Tables 3.2 – 3.5. Results are illustrated in Figures D.1 – D.23. Nitrosamines and precursors that were not detected in any samples collected during the experiments are not shown in the graphs.

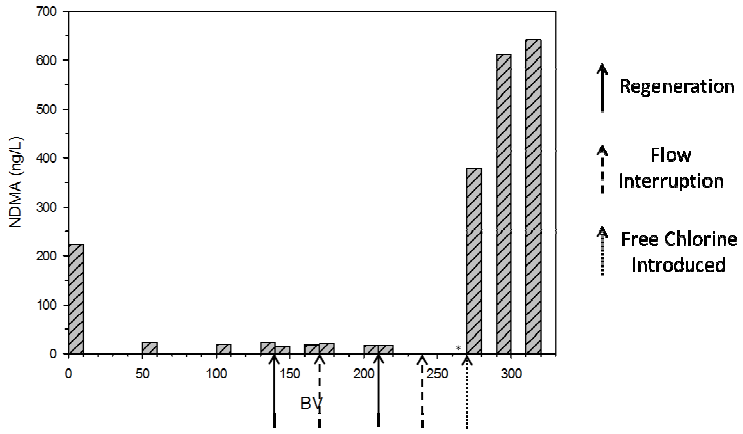


Figure D.1. NDMA release by Resin A300E during a continuous-flow column experiment. (* Indicates that a sample was taken and nitrosamines were below the LOQ.)

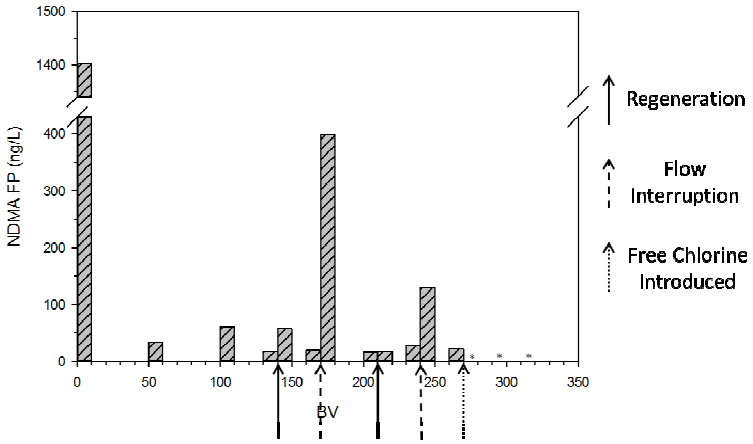


Figure D.2. NDMA precursor release by Resin A300E during a continuous-flow column experiment. (* Indicates that a sample was taken and nitrosamines were below the LOQ.)

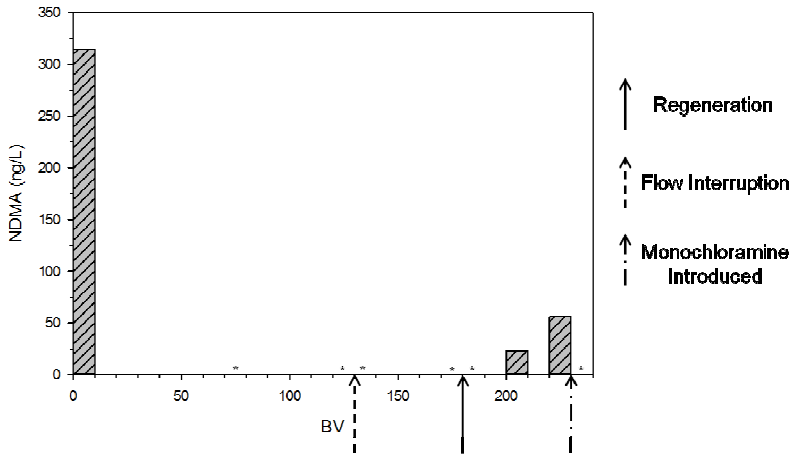


Figure D.3. NDMA release by Resin A400E in a continuous-flow column experiment. (* Indicates that a sample was taken and nitrosamines were below the LOQ.)

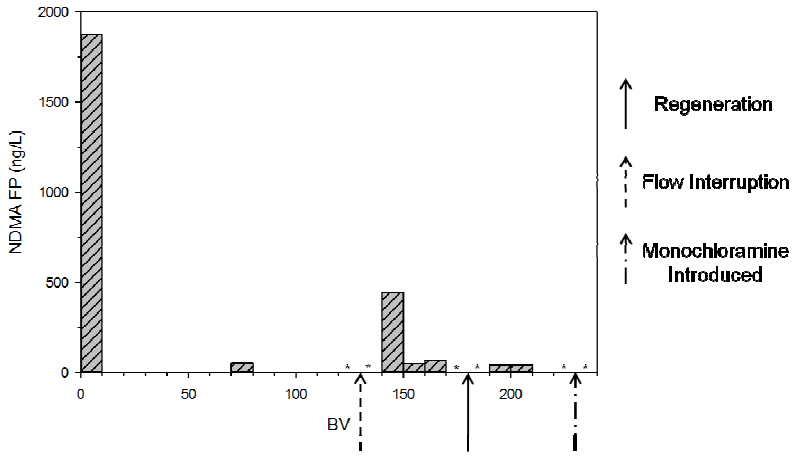


Figure D.4. NDMA precursor release by Resin A400E during a continuous-flow column experiment. (* Indicates that a sample was taken and nitrosamines were below the LOQ.)

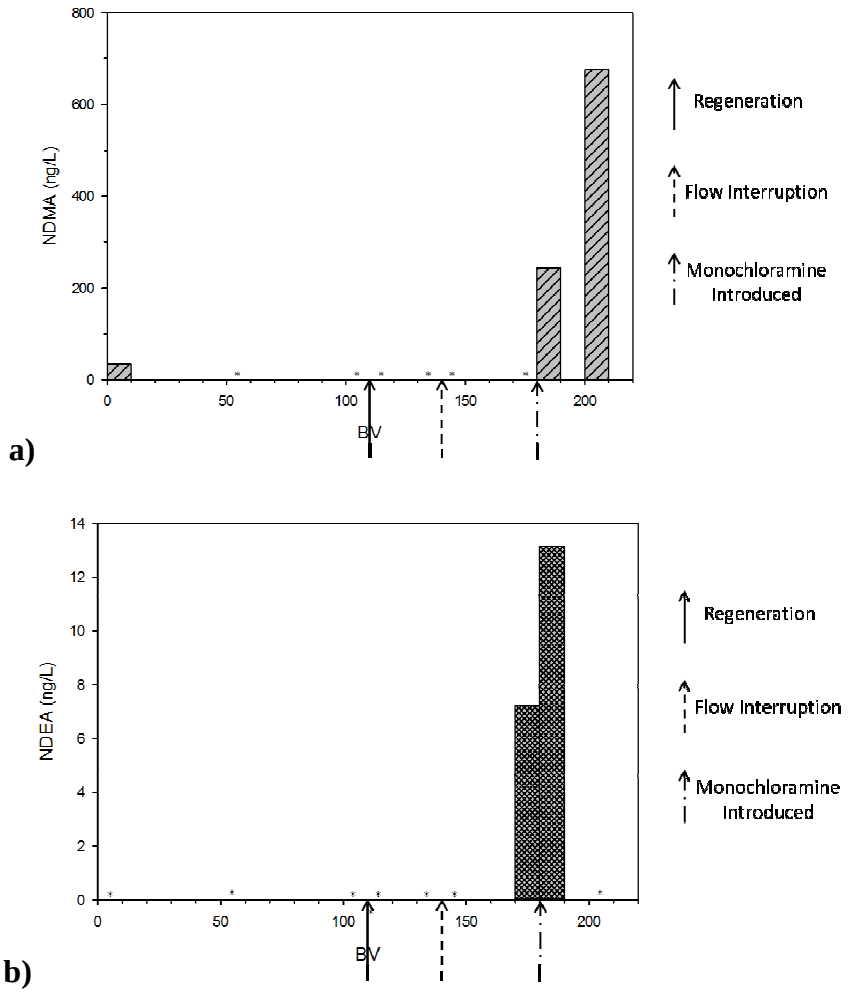


Figure D.5. Nitrosamine release by Resin A520E in a continuous-flow column experiment. a) NDMA release; b) NDEA release. (* Indicates that a sample was taken and nitrosamines were below the LOQ.)

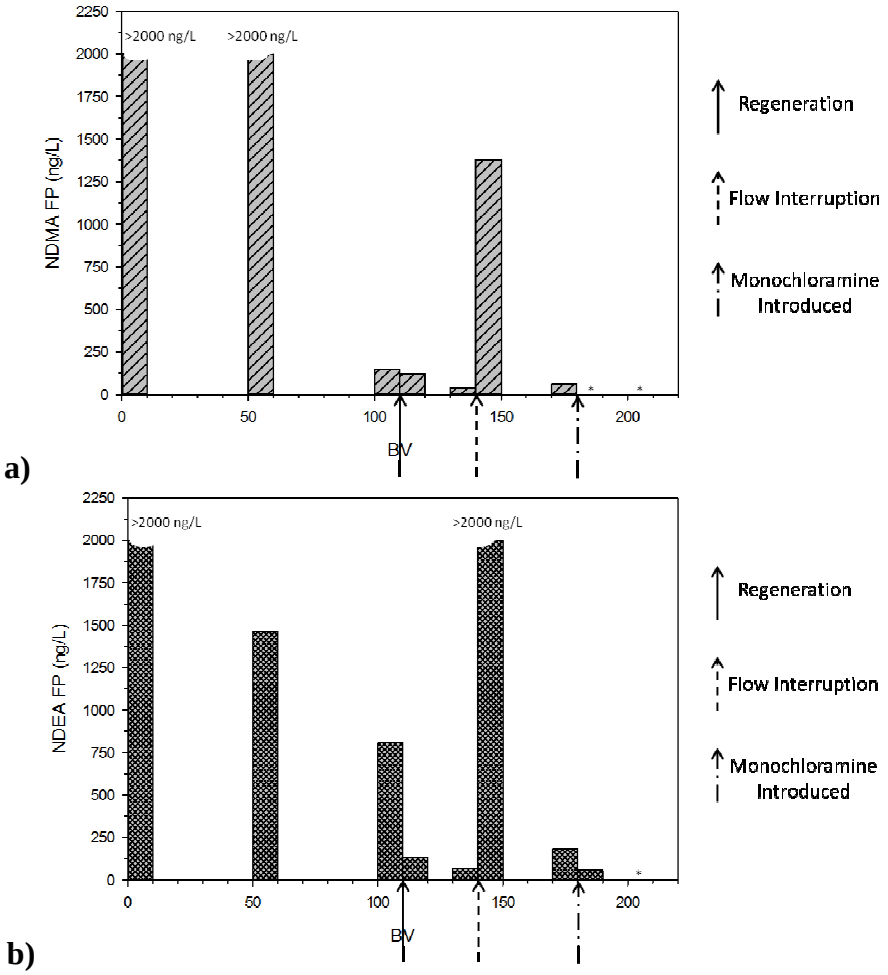


Figure D.6. Nitrosamine precursor release by Resin A520E during a continuous-flow column experiment. a) NDMA precursor release; b) NDEA precursor release. (* Indicates that a sample was taken and nitrosamines were below the LOQ.)

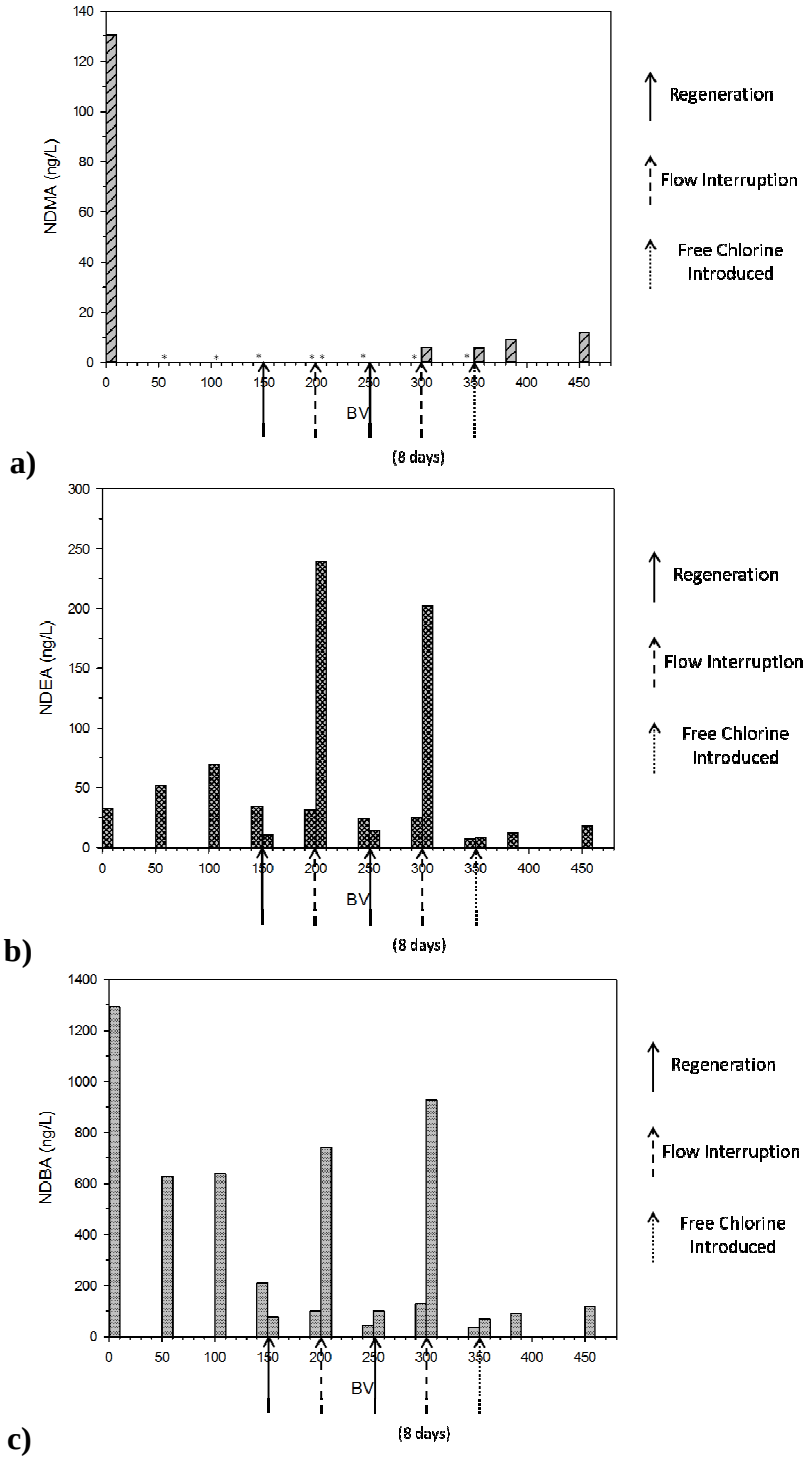


Figure D.7. Nitrosamine release by Resin A530E during a continuous-flow column experiment. a) NDMA release; b) NDEA release; c) NDBA release. (* Indicates that a sample was taken and nitrosamines were below the LOQ.)

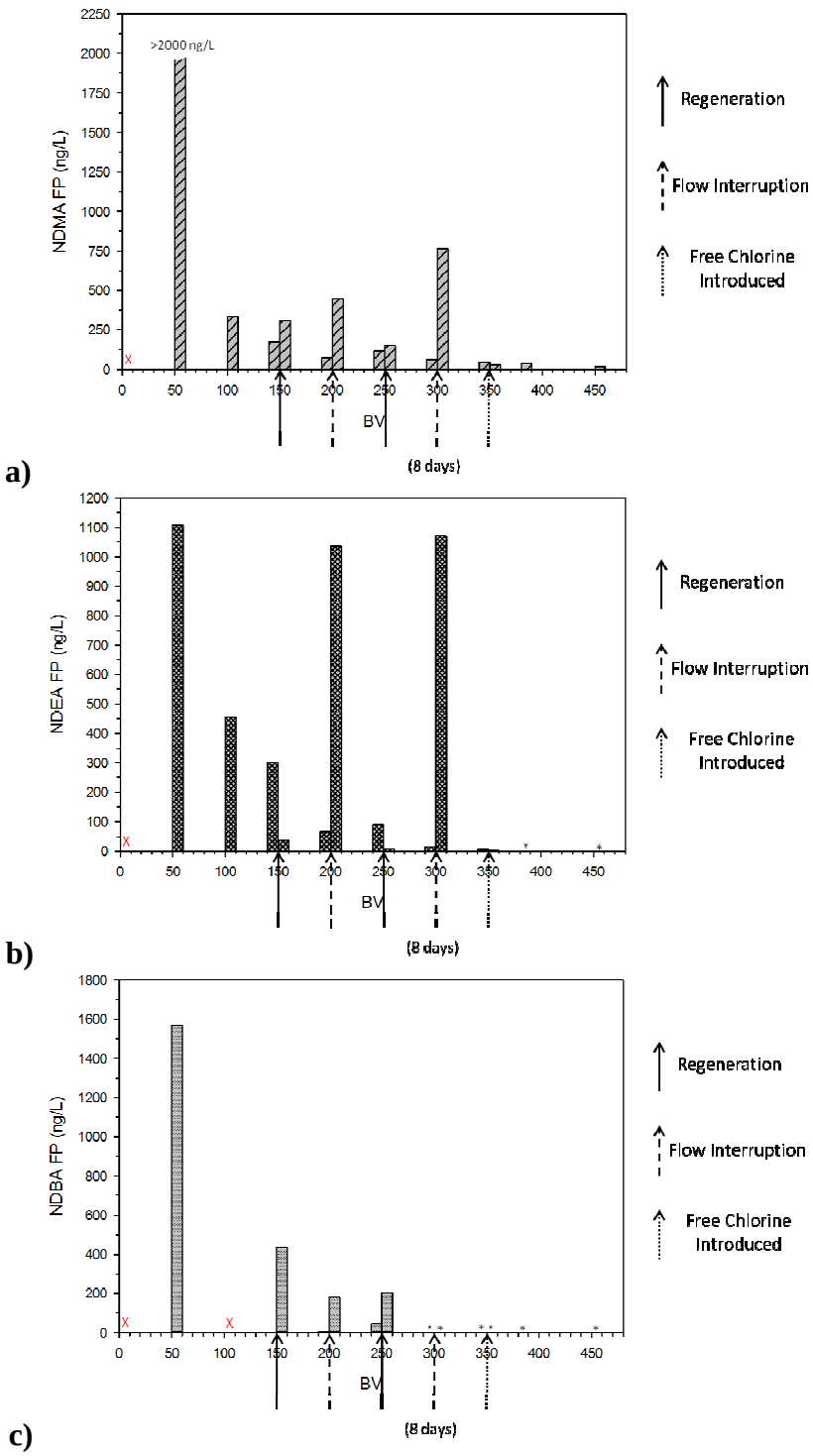


Figure D.8. Nitrosamine precursor release by Resin A530E during a continuous-flow column experiment. a) NDMA precursor release; b) NDEA precursor release; c) NDBA precursor release. (* Indicates that a sample was taken and nitrosamines were below the LOQ. X indicates that a sample was lost during processing.)

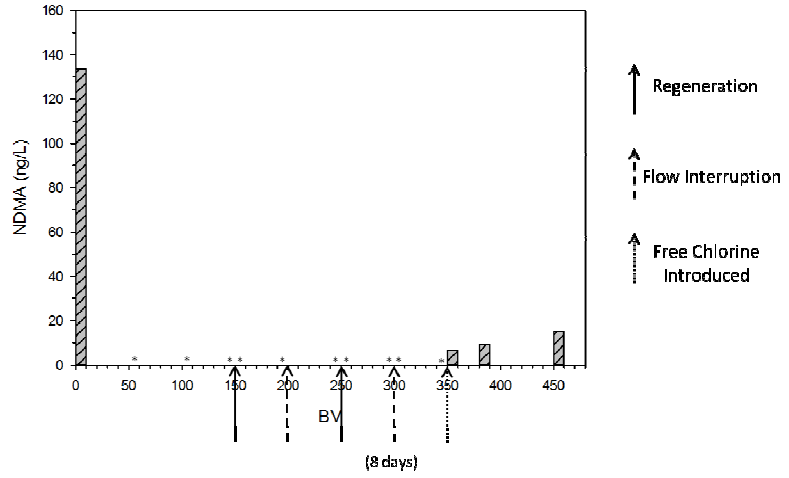


Figure D.9. NDMA release by Resin A600E during a continuous-flow column experiment. (* Indicates that a sample was taken and nitrosamines were below the LOQ.)

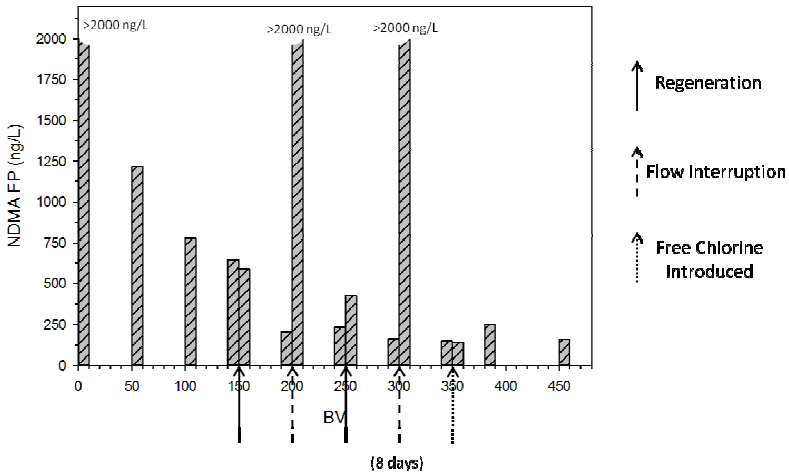


Figure D.10. NDMA precursor release by Resin A600E during a continuous-flow column experiment. (* Indicates that a sample was taken and nitrosamines were below the LOQ.)

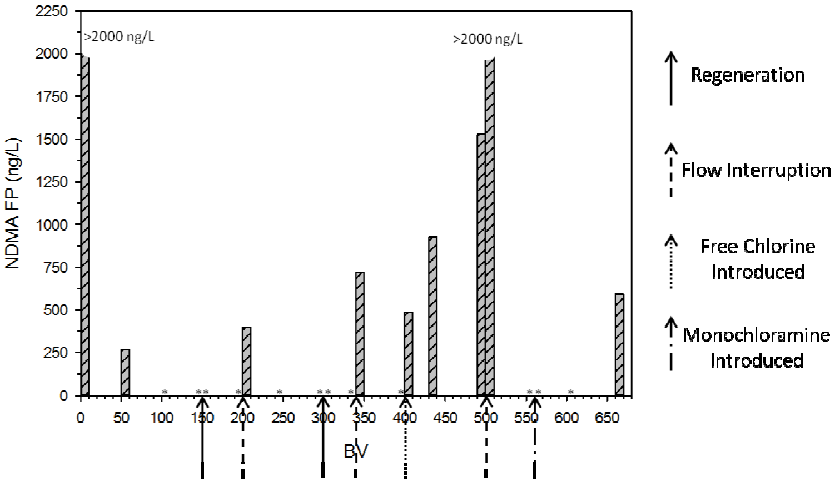


Figure D.11. NDMA precursor release by Resin A860E during a continuous-flow column experiment. (* Indicates that a sample was taken and nitrosamines were below the LOQ.)

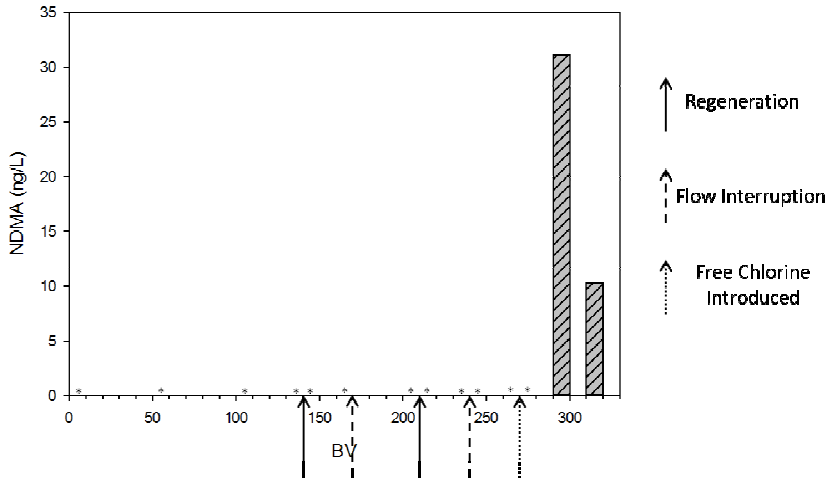


Figure D.12. NDMA release by Resin CalRes 2109 during a continuous-flow column experiment. (* Indicates that a sample was taken and nitrosamines were below the LOQ.)

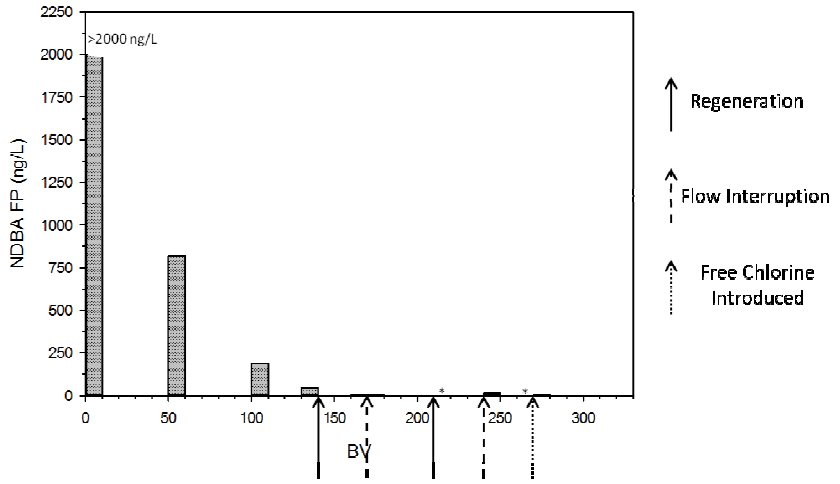


Figure D.13. NDBA precursor release by Resin CalRes 2109 during a continuous-flow column experiment. (* Indicates that a sample was taken and nitrosamines were below the LOQ.)

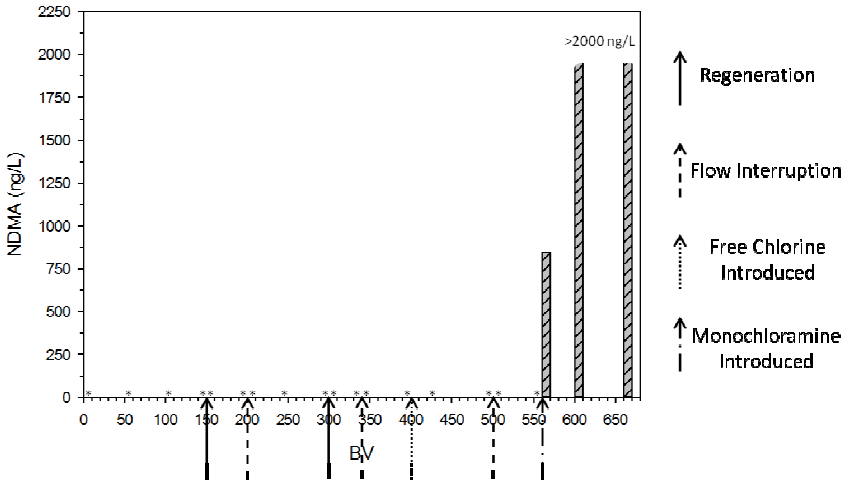


Figure D.14. NDMA release by Resin IRA400 during a continuous-flow column experiment. (* Indicates that a sample was taken and nitrosamines were below the LOQ.)

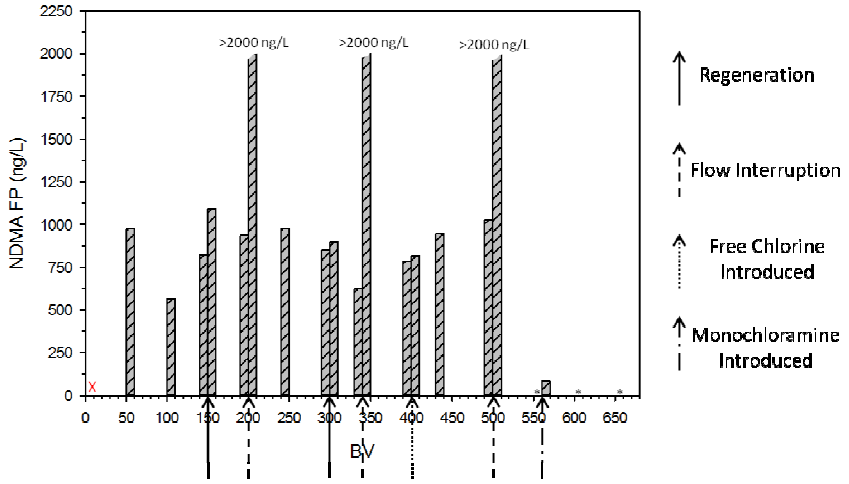


Figure D.15. Release of NDMA precursors by Resin IRA400 during a continuous-flow column experiment. (* Indicates that a sample was taken and nitrosamines were below the LOQ.)

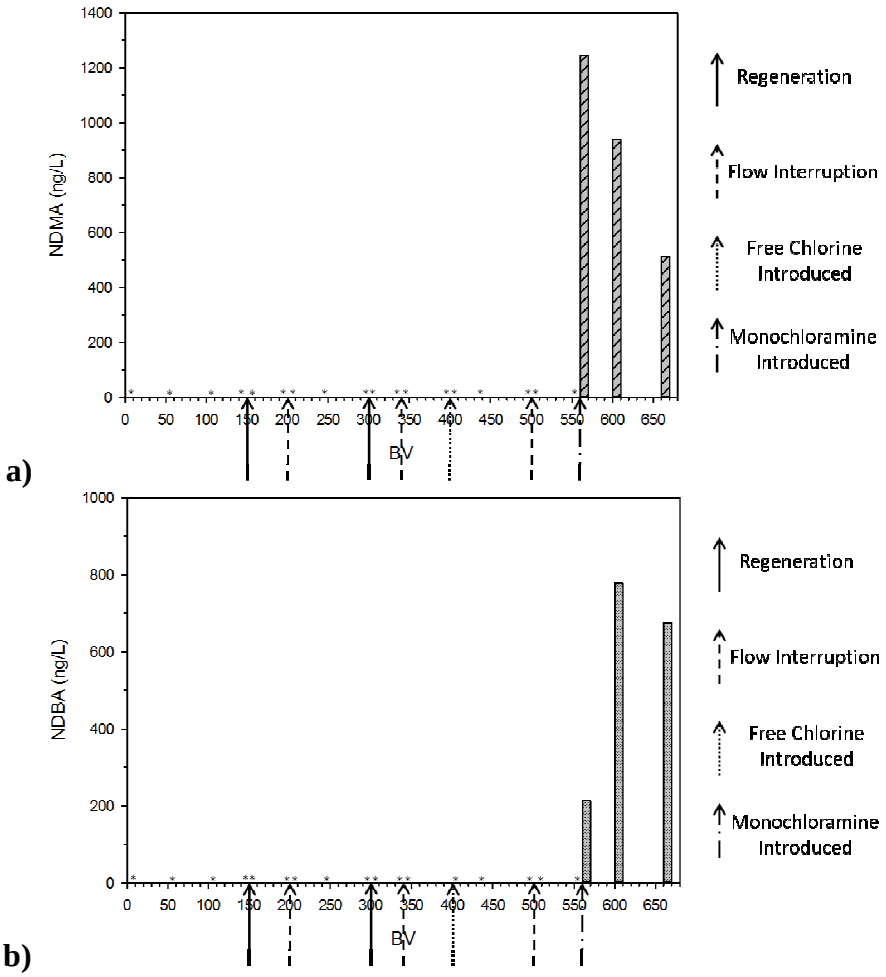


Figure D.16. Nitrosamine release by Resin PWA2 during a continuous-flow column experiment. a) NDMA release; b) NDBA release. (* Indicates that a sample was taken and nitrosamines were below the LOQ.)

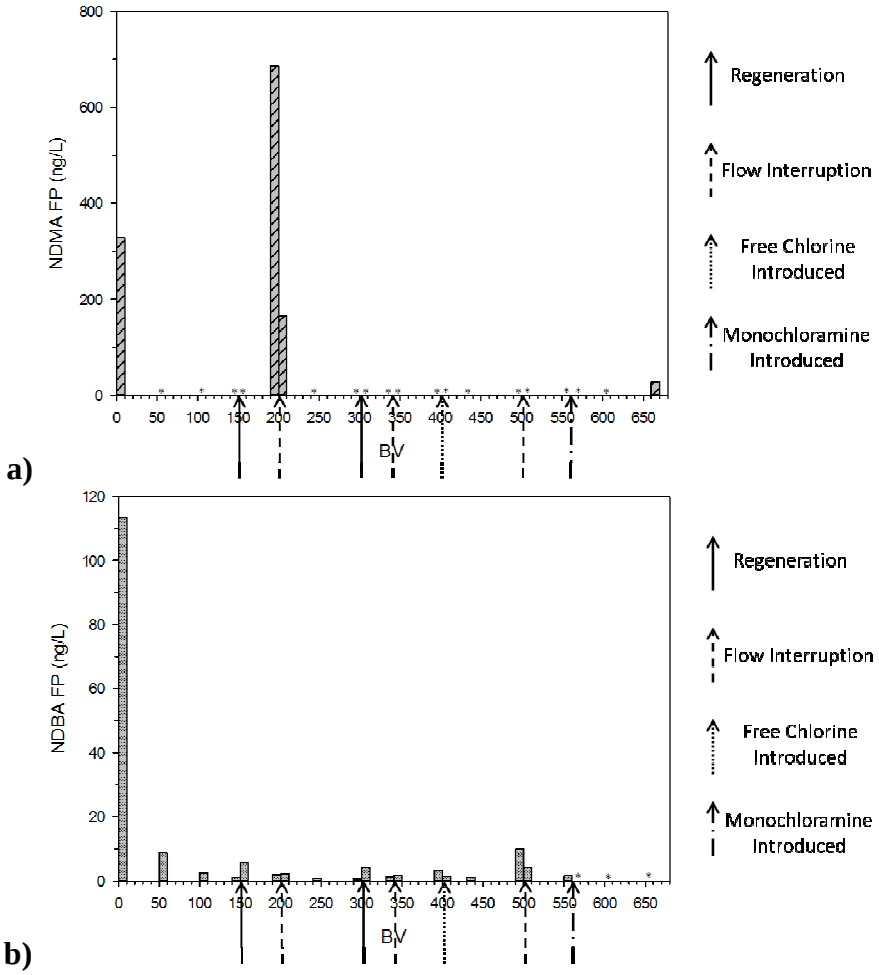


Figure D.17. Nitrosamine precursor release by Resin PWA2 during a continuous-flow column experiment. a) NDMA precursor release; b) NDBA precursor release. (* Indicates that a sample was taken and nitrosamines were below the LOQ.)

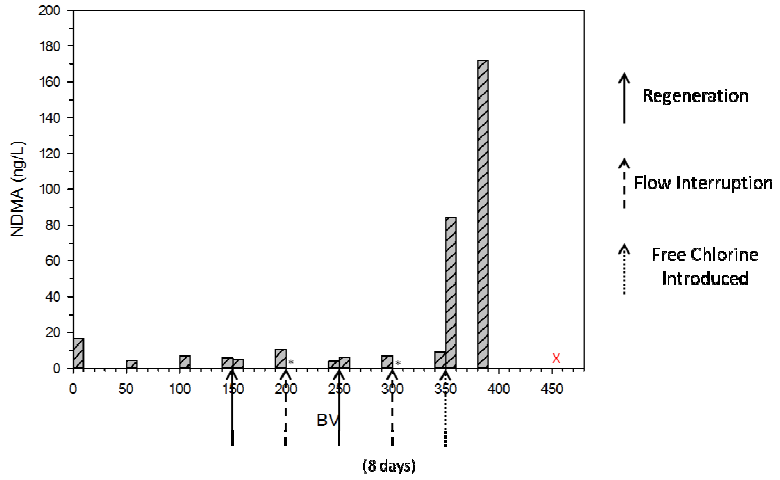


Figure D.18. NDMA precursor release by Resin PWA5 during a continuous-flow column experiment. (* Indicates that a sample was taken and nitrosamines were below the LOQ.)

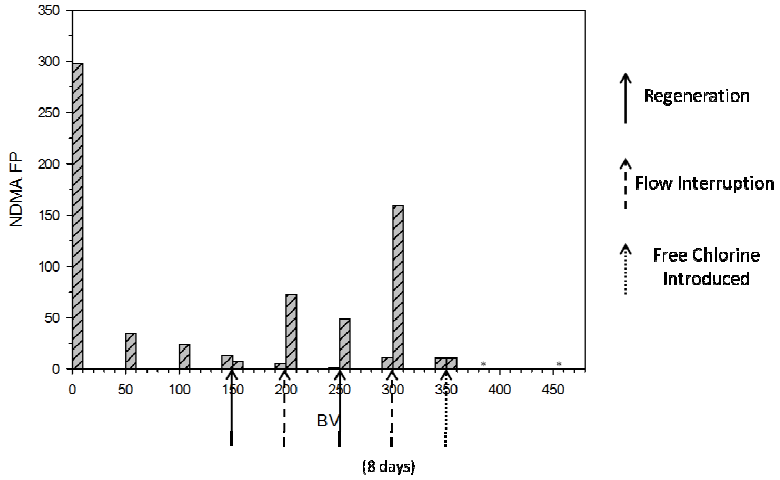


Figure D.19. NDMA precursor release by Resin PWA5 during a continuous-flow column experiment. (* Indicates that a sample was taken and nitrosamines were below the LOQ.)

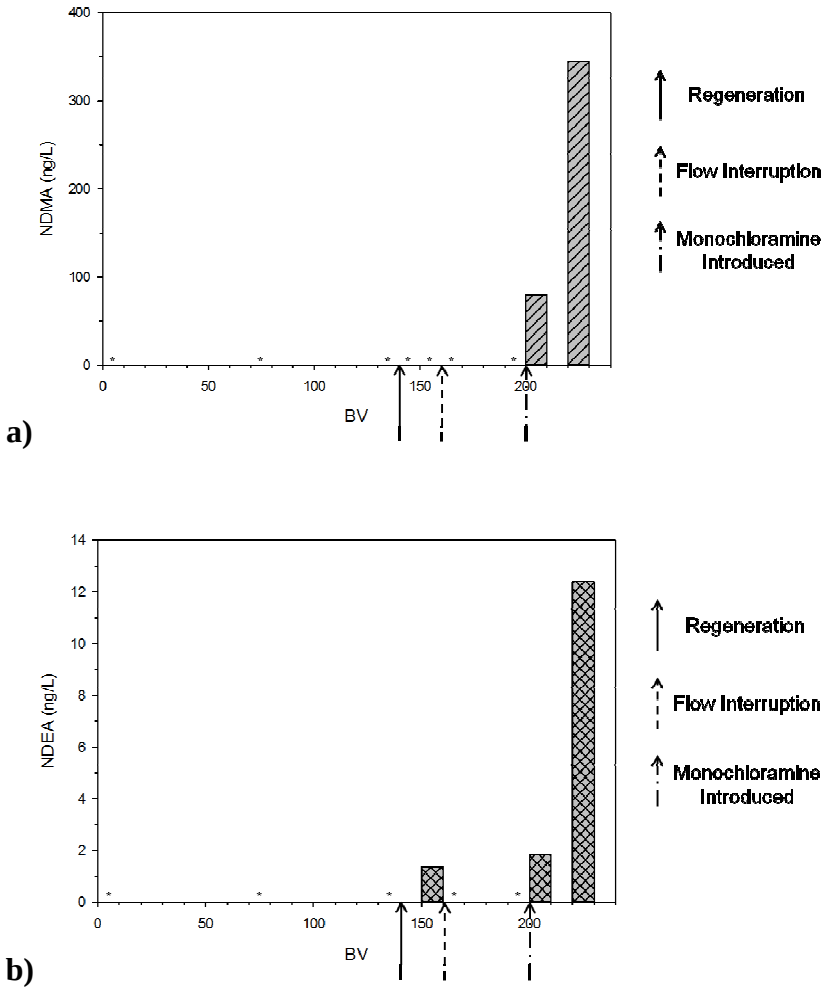


Figure D.20. Nitrosamine release by Resin SIR-100 during a continuous-flow column experiment. a) NDMA release; b) NDEA release. (* Indicates that a sample was taken and nitrosamines were below the LOQ.)

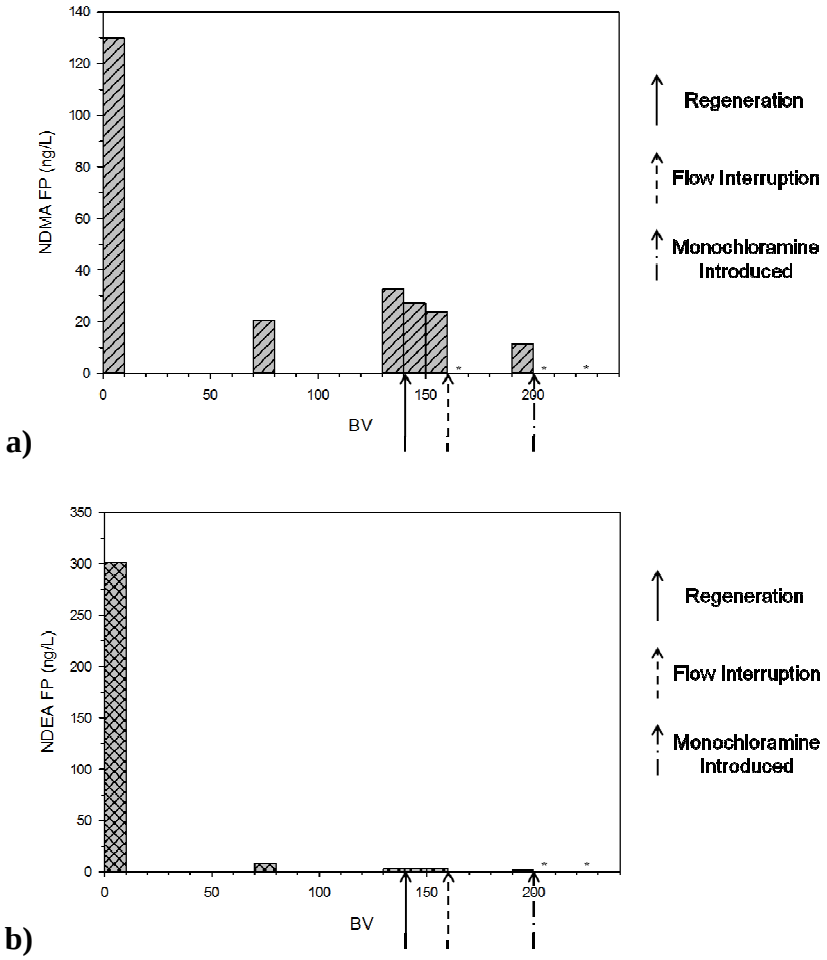


Figure D.21. Nitrosamine precursor release by Resin SIR-100 during a continuous-flow column experiment. a) NDMA precursor release; b) NDEA precursor release. (* Indicates that a sample was taken and nitrosamines were below the LOQ.)

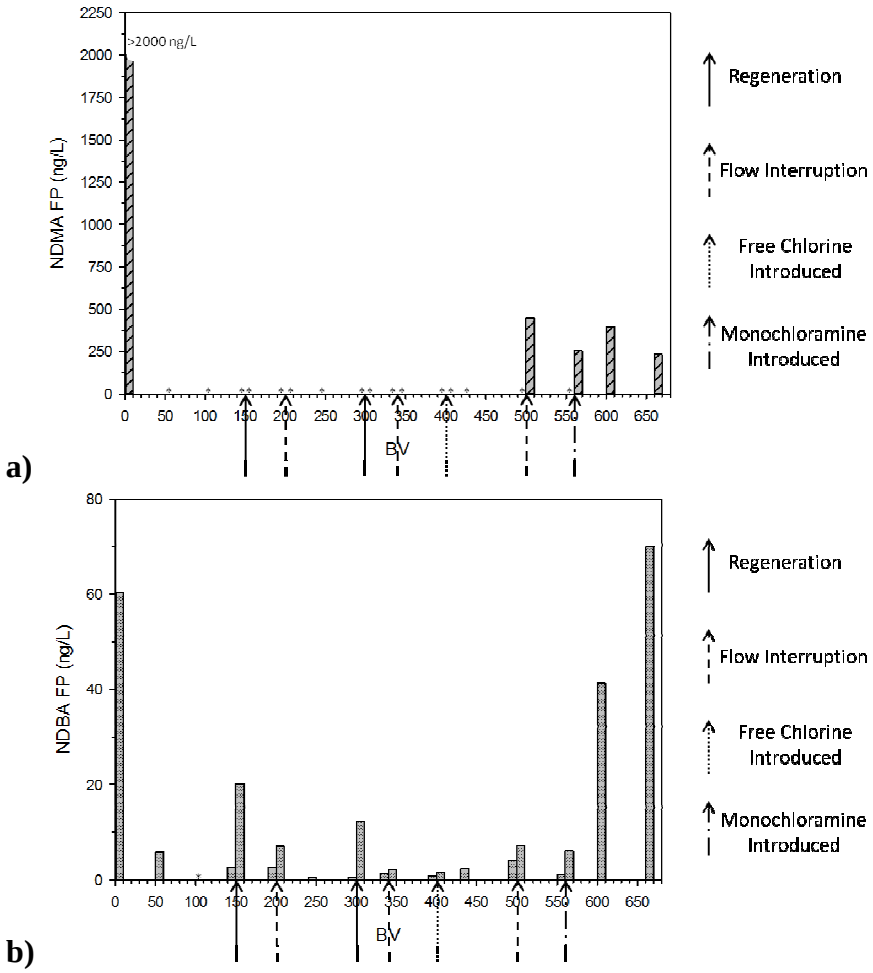


Figure D.22. Nitrosamine precursor release by Resin SIR-110 during a continuous-flow column experiment. a) NDMA precursor release; b) NDBA precursor release. (* Indicates that a sample was taken and nitrosamines were below the LOQ.)

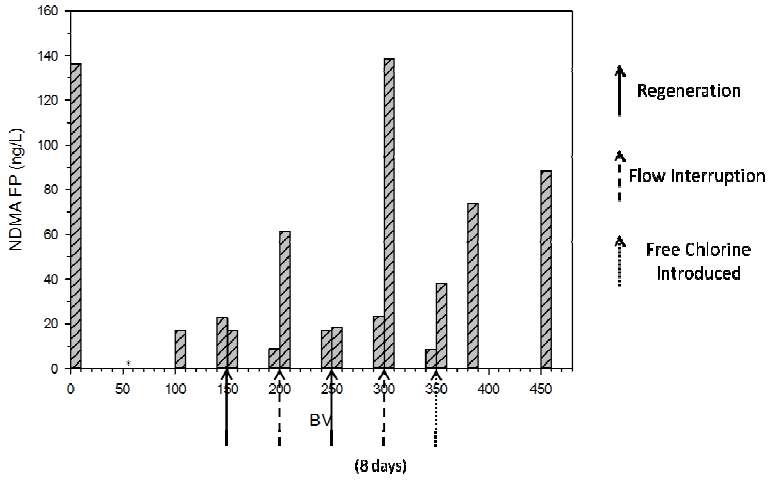


Figure D.23. NDMA precursor release by Resin TAN-1 during a continuous-flow column experiment. (* Indicates that a sample was taken and nitrosamines were below the LOQ.)

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