# Measurement of Nitrophenols in Rain and Air by Two-Dimensional Liquid Chromatography−Chemically Active Liquid Core Waveguide Spectrometry

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We report a novel system to analyze atmospheric nitrophenols (NPs). Rain or air sample extracts (1 mL) are preconcentrated on a narrow bore (2 mm) aliphatic anion exchanger. In the absence of strong retention of NPs exhibited by aromatic ion exchangers, retained NPs are eluted as a plug by injection of 100 $\mu$L of 0.1 M Na$_2$SO$_4$ on to a short (2 × 50 mm) reverse phase C-18 column packed with 2.2 $\mu$m particles. The salt plug passes through the C-18 column unretained while the NPs are separated by an ammonium acetate buffered methanol−water eluent, compatible with mass spectrometry (MS). The eluted NPs are measured with a long path Teflon AF-based liquid core waveguide (0.15 × 1420 mm) illuminated by a 403 nm light emitting diode and detected by a monolithic photodiode-operational amplifier. The waveguide is rendered chemically active by suspending it over concentrated ammonia that permeates into the lumen. The NPs ionize to the yellow anion form ($\lambda_{max} \sim 400$ nm). The separation of 4-nitrophenol, 2,4-dinitrophenol, 2-methyl-4-nitrophenol, 3-methyl-4-nitrophenol, and 2-nitrophenol (these are the dominant NPs, typically in that order, in both rain and air of Houston and Arlington, TX, confirmed by tandem MS) takes just over 5 min with respective S/N = 3 limits of detection (LODs) of 60, 12, 30, 67, and 23 pg/mL compared to MS/MS LODs of 20, 49, 11, 20, and 210 pg/mL. Illustrative air and rain data are presented.

Environmental occurrence of nitrophenols (NPs) was first reported 35 years ago;[1,2] their toxicity to plants and humans has since led to continued attention.[3-6] Many NPs (especially 3-methyl-4-nitrophenol (3-Me-4-NP)) are potent vasodilators;[7] 2-NP can reduce the oxygen carrying capacity of blood;[8] 4-NP and 2,4-dinitrophenol (2,4-DNP) are cytotoxic, mutagenic, and likely carcinogenic.[9] 4-NP, routinely found in diesel exhaust aerosols, is both estrogenic and antiandrogenic.[10] Many NPs cause headache, shortness of breath, nausea, fever, and peripheral numbness.[1] Some NPs affect plant cell metabolism even at a 10 $\mu$M concentration by uncoupling oxidative phosphorylation;[11] some decrease transpiration[12] and inhibit uptake of nutrients[13] and growth.[14] Phytotoxicity of NPs may contribute to forest decline;[11] compared to healthy leaves, higher NP levels are found on damaged ones.[15] NPs are also toxic to algae and fish.[16]

Atmospheric NPs have both primary and secondary sources.[8] Primary sources include industrial raw materials or intermediates involved in the manufacturing of plastics, pharmaceuticals, disinfectants, dyes, explosives, herbicides, and insecticides; the sources stem from the use or disposal of these products, combustion of coal and wood, and notably, internal combustion engine exhaust.[3,17] Secondary formation of NPs occurs atmospherically via sequential reactions of aromatics with •OH and

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NO$_2$ in the daytime and NO$_3^\bullet$ and NO$_2$ in the nighttime.[18−20] In the aqueous phase, NPs can be formed from phenols by dissolved HONO photolysis.[21] A comparison of atmospheric benzene, toluene, xylenes, and ethylbenzene in air and the corresponding NPs in rain suggest more rapid conversion of alkylbenzenes to NPs than benzene,[22] as would be expected from their $^\bullet$OH reactivities.

Atmospheric NPs occur in aqueous, gaseous, and particulate forms. Concentrations of ng-$\mu$g/m$^3$ have been reported;[15,23−27] they are distributed globally, and this includes remote regions.[15,24,27] Among atmospheric NPs, 4-NP, 2-NP, and 2,4-DNP are reportedly the major contributors. Our interest in atmospheric NPs lies in that NPs may act as reservoirs for HONO. Much as they may form from HONO by photolysis,[21] they also release HONO by photolysis over a broad range of wavelengths.[28] A lot is unclear about why morning ozone peaks are observed in some major metropolitan areas,[29] and NPs, via HONO, may provide the missing $^\bullet$OH source whereas HONO concentration by itself is inadequate. In this context, extant measurements of NP virtually all come from Europe; limited measurements made in the U.S. are now 25 years old.[5,30]

## MEASUREMENT STRATEGIES

In the following, the general literature on the measurement of NPs is briefly surveyed. The majority of the extant approaches rely on extraction followed by chromatography-MS. More recent strategies describe adsorption on XAD-7 sorbent, elution with some organic solvent and analysis by liquid chromatography-atmospheric pressure chemical ionization mass spectrometry (LC-APCI-MS),[31] extraction with polyacrylate solid phase microextraction fibers, conversion to the *t*-butyldimethylsilyl derivative followed by GC/MS,[32] liquid−liquid extraction, and LC-APCI-MS/MS;[22] and solid phase extraction[26,33] or supported liquid membrane microextraction[34] followed by LC-UV. Using a dynamic

extractant film of *n*-butyl chloride in octanol, Miro et al.[35] was able to more sensitively measure several NPs simultaneously by multiwavelength spectrometry and multiple linear regression than in an earlier similar effort.[36] Lüttke et al.[24] separated cloudwater with an impactor and collected the NPs in the effluent gas by a mist chamber. They processed both the cloudwater and the gas phase extract by acidification, NaCl addition, sorption by a C$_{18}$ sorbent, elution by ethyl acetate, and analysis by isotope dilution GC/MS. Hoffmann et al.[37] concentrated NPs in cloudwater and rainwater into methyl *t*-butyl ether (MTBE) by a novel extraction apparatus and carried out LC-ion trap MS/MS$^n$. Leuenberger et al.[5] collected aerosols on glass fiber filters and (semi-) volatiles on a downstream polyurethane foam plug and Tenax-GC for gaseous constituents alone, followed by solvent extraction/thermal desorption GC/MS. Hinkel et al.[6] measured NPs on plant surfaces by acidic dichloromethane extraction, diazomethane derivatization, and GC/MS.

Other methods, from enzyme-linked immunoassay (ELISA[38]) to differential pulse voltammetry on various electrodes,[39,40] have all been used. Amperometry has been used in the batch[41,42] or the flow injection mode[43] and following capillary LC[44] or electrophoretic[45] separation. 4-NP is often used as a tag in ELISA where an alkaline phosphatase cleaves a *p*-nitrophenyl phosphate linkage; several of the above approaches target the liberated 4-NP for measurement. One approach measures the loss of fluorescence as 4-NP begins to absorb radiation around 400 nm that otherwise excites a fluorescent coumarin dye.[46]

The approaches above are not configured for automated field use. Most are not sensitive or robust enough for the purpose. Some amperometric methods report excellent sensitivity but require too frequent electrode maintenance in practice. Chromatography coupled to mass spectrometry, especially MS/MS techniques, have excellent sensitivity and selectivity but are hardly readily fieldable. MS-based approaches provide unequivocal confirmation of identity but accurate quantitation requires expensive isotopically labeled standards. Considerable capital, operating, and maintenance costs further deter wide application.

Prior experience in designing and fielding instruments to measure soluble gases/particles with liquid/ion chromatography approaches[47,48] predisposed us to a similar approach, especially as NPs, like inorganic salts, are water-soluble. However, unlike

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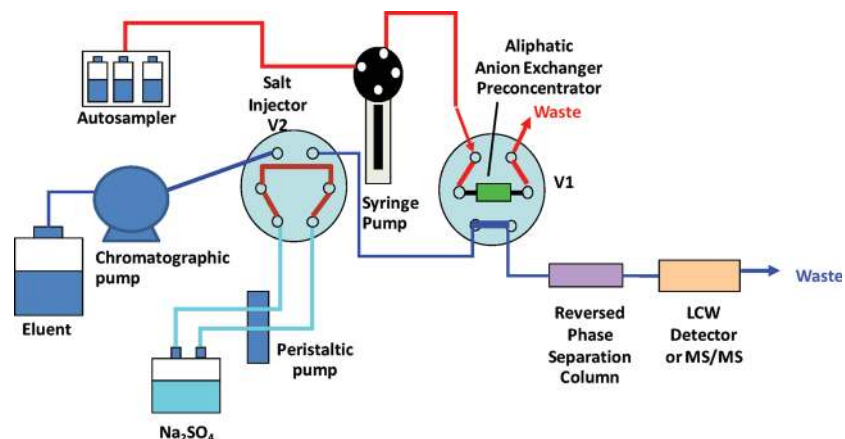(48) Ullah, S. M. R.; Takeuchi, M.; Dasgupta, P. K. *Environ. Sci. Technol.* **2006**, *40*, 962–968.

**Figure 1.** General experimental setup.

suppressed conductometry for ionic solutes, there are no selective detection schemes for NPs. We considered that like nitroanilines (basis of the Hammett acidity scale[49]), all NPs are also acid−base indicators, except that they are weaker acids than nitroanilines. NPs turn yellow in base and absorb strongly around ~400 nm; few other water-soluble atmospheric compounds absorb in the visible region. A long path liquid core waveguide (LCW) cell may provide sufficient absorbance detection sensitivity;[50] to provide further selectivity, we sought to exploit the dual nature of NPs (ionic: can be preconcentrated on anion exchange media; hydrophobic: can be separated on reverse phase media) and, thus, provide a 2-dimensional separation. Aqueous NPs can be preconcentrated on anion exchangers, eluted as a plug by salt to a reverse phase column where separation can be conducted with a standard electrospray ionization/mass spectrometry (ESI/MS)-compatible eluent. Instead of ESI/MS, however, LCW-based absorbance can be routinely measured after base introduction to ensure ionization of NPs. To further identify NPs, it will be possible to perform detection with and without basification while the ESI/MS-compatible eluent will allow MS confirmation without method changeover. We describe the results of such an approach.

## EXPERIMENTAL SECTION

**Reagents and Materials.** These were obtained from standard suppliers; please see Supporting Information.

**Rain Collection.** Rain samples were collected using a sequential wet-only rain sampler (*Rain-go-round*, www.horiba.com) that collects rain in 5 mL increments through a 46.5 cm² opening; this provides a ~1.1 mm resolution between samples. The sampler was set in an open area at the University of Texas at Arlington, ~9.2 m above ground level, away from any roof projections. Samples were stored at −20 °C until analysis.

**Air Sampling.** Sampling cartridges consisted of 1 g 35−60 mesh silica gel in three-eighths in. i.d. polypropylene tubes with glass wool end retainers; terminal barbed fittings for one-eighth in. i.d. tubes were capped after filling. Poly(tertrafluoro)ethylene (PTFE) tubes were used throughout.

A Labview-controlled 24-channel sampler was used for sampling through an inverted glass funnel inlet at 2 standard liters/

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min (SLPM) sequentially through each cartridge for 1 h; the main manifold flow was 20 L/min to minimize line losses. The sampler was located atop a 17-story building on the University of Houston campus (Houston, TX) in April to May of 2009. Every 24 h, cartridges were replaced and sampled ones capped and stored in sealed bags at −20 °C until analysis.

**Standard Gaseous Nitrophenol Calibration Source.** We made permeation tubes individually filled with solid 2-NP and 5-MeO-2-NP and gravimetrically calibrated them. Known concentration streams of adjustable humidity were generated by dilution; see description and Figures S1 and S2 in the Supporting Information.

**Sample Preparation.** Frozen rain samples were allowed to reach room temperature and filled in autosampler vials through 0.45 $\mu$m pore size nylon syringe filters; some were spiked in addition to check recovery. Frozen sampled cartridges were kept at room temperature for 2 h and then were eluted with 2 mL of 50% v/v methanol. The eluate was diluted to 4 mL with Milli-Q water. This ~<25% methanolic solution was filtered and loaded into autosampler vials. Standard stock (100 mg/L) NP solutions prepared in 10 mM $Na_2CO_3$ were diluted serially with 25% v/v methanol to prepare working standards. Milli-Q water and field blank cartridges were, respectively, used as controls for rain and air samples.

**Two-Dimensional Preconcentration and Separation.** The general arrangement shown in Figure 1 uses a chromatographic pump (GS-50, this and all columns from www.dionex.com) and a programmable syringe pump (V6, www.kloehn.com). The latter delivered 1 mL of sample at 0.48 mL/min from the autosampler to an anion exchanger preconcentrator (AG21, 2 × 50 mm) contained within the loop of 6-port injector V1 (shown in the loading mode). Meanwhile, the 100 $\mu$L loop of a second 6-port valve V2 is filled with an eluent plug of 100 mM $Na_2SO_4$ in 4 mM $NH_4OAc$/42% v/v MeOH. Both V1 and V2 are switched simultaneously. The chromatographic pump delivers the salt plug from V2 to the preconcentration column, and the sample is eluted to the reverse phase separation column (Acclaim-120 C-18, 2.2 $\mu$m, 2.1 × 50 mm) that separates the solutes by a different retention mechanism. The isocratic eluent program uses 4 mM $NH_4OAc$/42% v/v MeOH. As real samples were analyzed, we incorporated a wash step with methanol prior to sample injection. A 10-port valve was used for V2, and using a second loop, 250 $\mu$L of methanol was injected prior to any
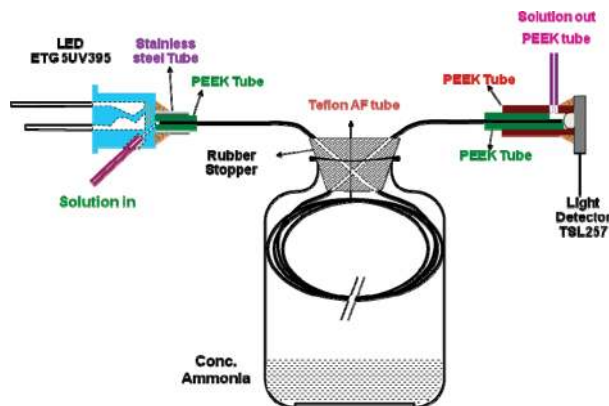
**Figure 2.** Chemically active liquid core waveguide absorbance detector.

analysis. Later, since the pump was gradient capable, we used a binary eluent with $A = 10$ mM aqueous $NH_4OAc$ and $B = 70\%$ v/v $MeOH/H_2O$; normally, an isocratic composition of 60% B was used; except at the beginning of each analytical cycle, a triangular pulse of B ($t = 0 \rightarrow 1 \rightarrow 2$ min, %B $= 60 \rightarrow 100 \rightarrow 60$) was used to remove strongly retained components. The analytical cycle, operated under control of Peaknet V6.0 software, was <10 min, and could be completed in as little as 7 min.

**Chemically Active Liquid Core Waveguide (CA-LCW) Detector.** Figure 2 shows the general arrangement. A 0.15 mm i.d × 1420 mm long Teflon AF capillary is coupled to a 403 nm light emitting diode LED at one end; the other end of the AF tube was coupled to the hemispherical ball lens of a photodiode. Details are given in the Supporting Information; liquid inlet/outlet connections were made through the LED and the photodiode coupling. All but 10 cm at each end of the AF tube was put within a 50 mL capacity polypropylene jar containing ~25 mL of concentrated ammonia at the bottom, diluted 1:1 with water. Ammonia transfers through the highly permeable[51,52] AF tube making the LCW chemically active and raising the pH of the internal solution.

**Tandem Mass Spectrometry.** We used a TSQ Quantum Discovery Max triple-quadrupole mass spectrometer (www.thermo.com) in the negative electrospray ionization mode with a heated electrospray ionization probe maintained at 325 °C. The vaporizer and capillary temperatures were 270 and 350 °C, respectively, with an electrospray voltage of 4000 V. A programmed diversion valve was used to direct the LC output to the MS only in desired time windows. Fragmentation and monitoring details for specific analytes are given in the Supporting Information.

## RESULTS AND DISCUSSION

**Selectivity and Dimensionality in Preconcentration and Separation.** Too many compounds in air and rain absorb in the UV region. NPs, however, absorb strongly in the visible region, and few atmospheric compounds show such indicator behavior. Still, one would wish to preconcentrate NPs selectively before analysis. As indicated, we investigated preconcentration by anion exchange, plug elution with a salt and separation by a different retention mechanism. We initially chose separation columns that

provide both anion exchange and hydrophobic retention (PAX-100, PAX-500, WAX-1). With ESI/MS compatible eluents, most NPs were retained too strongly. In contrast, reverse phase columns provided attractive separations; similar reports are in the literature (see introduction). We chose a short, narrow bore, microparticulate ($2 \times 50$ mm, 2.2 $\mu$m) C-18 column that separated all the major NPs in air and rain at our location (vide infra) in ~5 min.

Affecting plug elution of NPs preconcentrated by anion exchange proved difficult. Most anion exchangers have aromatic skeletons, and the $\pi-\pi$ interaction with the NPs are too strong to accomplish plug elution with any reasonable concentration and volume of a salt plug. We considered acrylate and polyvinyl skeleton anion exchangers, but none were available as short columns. Anion exchangers based on the amine-diepoxide chemistry[53,54] were suggested to us. Up to 1 mL of the mixture of test NPs spiked in a rain matrix or in 25% methanol (representing air sampling cartridge eluate) was quantitatively captured by such a column (AG21, Dionex), and plug elution of these on to a C-18 column by 100 $\mu$L of 100 mM $Na_2SO_4$ was readily possible. The salt plug actually promoted the retention of the highly polar DNP on the C-18 column.

**CA-LCW Detection Strategy.** Often, chromatography/reaction is optimal at one pH, but detection is optimal at another. Earlier, we solved an analogous problem by introducing $NH_3$ through a membrane prior to detection;[55] other reagents have also been introduced without dilution.[56] With Teflon AF, analytes have been deliberately preconcentrated into the walls of a long path cell[57] or a volatile background removed;[58] other membranes have also been used for this latter purpose.[59] Presently, an elevated pH improves detection by completing ionization. However, raising the eluent pH would have affected the separation and likely adversely affected the column. The unusual properties of Teflon AF offered a unique opportunity to directly permeate $NH_3$ into the waveguide and render it "chemically active".

The measured pH of the methanolic eluent is ~6.7; the available $pK_a$ values stated below are in water,[60] limiting the interpretation. Nevertheless, the ionization of 2,4-DNP ($pK_a$ 3.94) will be complete, but that of 4-NP ($pK_a$ 7.08), 2-NP ($pK_a$ 7.23), 3-Me-4-NP ($pK_a$ 7.33), and 2-Me-4-NP ($pK_a$ not listed, should be similar to 3-Me-4-NP) will be incomplete. For conditions where the absorption from the unionized NP is negligible, it is readily shown (see Supporting Information) that the ratio ($R$) of the signals ($S_{fin}$ and $S_{in}$) at the different pH levels ($pH_{fin}$ and $pH_{in}$) is given by

$$R = S_{fin}/S_{in} = (K_{In}+H_{in})/(K_{In}+H_{fin})\dots \quad (1)$$

where $K_{In}$ is the dissociation constant of the NP and $H_{in}$, $H_{fin}$ are the hydrogen ion concentrations corresponding respectively

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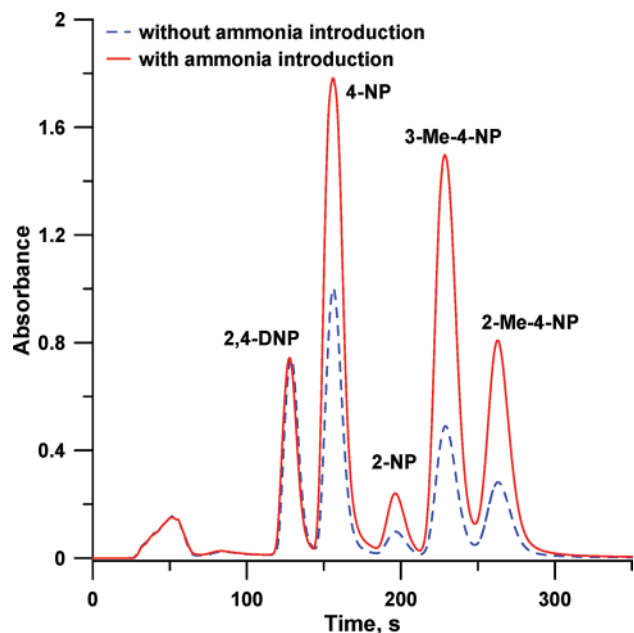(53) Pohl, C. A.; Saini, C. U.S. Patent 7,291,395. November 6, 2007.
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**Figure 3.** Chromatogram of a standard mixture of NPs with and without ammonia introduction through the LCW. Concentrations in order of elution: 4, 8, 4, 8, and 4 ng/mL, respectively.



**Figure 4.** Calibration series for the dominant NPs.

to $pH_{in}$, $pH_{fin}$. A chromatogram of several test NPs with and without ammonia introduction is shown in Figure 3. The observed ratios (in the order they elute) are 1, 1.8, 2.6, 3.2, and 2.9. The order of the first four is consistent with the $K_{In}$ values. One would predict that 2-Me-4-NP will have a $pK_a$ value in 42% methanol between those of 2-NP and 3-Me-4-NP.

Initially, we planned splitting the column effluent into two LCW detectors, to measure one with $NH_3$ introduction and measure the other without (or with HCl introduction) and, thus, establish an added measure of selectivity/identification. Experience with actual samples indicated, however, that the preconcentration/elution strategy and the spectral window together provide such selectivity that the observed signal after $NH_3$ introduction was entirely due to a specific NP. This was confirmed by MS identification, rendering dual LCW detection superfluous.

The use of long path LCWs increase detection sensitivity, but too large an LCW volume will result in loss of efficiency. The present case is complex, however, as discussed in the Supporting Information (Figure S3, Table S1, and accompanying discussion), efficiency can actually increase with increased LCW length for some analytes up to a point. Theoretical and practical considerations surrounding the optimum length/volume of an LCW detector will be addressed elsewhere.

**Calibration Behavior and Detection Limits.** CA-LCW detected calibration chromatograms of the dominant NPs appear in Figure 4; the corresponding area-based calibration plot is shown in Figure S3 in the Supporting Information. On the basis of the S/N = 3 criterion, the respective limits of detection (LODs) for 2,4-DNP, 4-NP, 2-NP, 3-Me-4-NP, and 2-Me-4-NP were 12, 60, 23, 67, and 30 pg/mL. Mass LODs are the same numerical values in pg and compare with MS/MS LODs of 49, 20, 210, 20, and 11 pg, respectively, under otherwise identical conditions. For comparison, Hoffmann et al. have reported MS/MS LODs of 50−100 pg for various NPs after MTBE extraction. It is remarkable that the CA-LCW containing ~$25 of electronics is capable of providing LODs

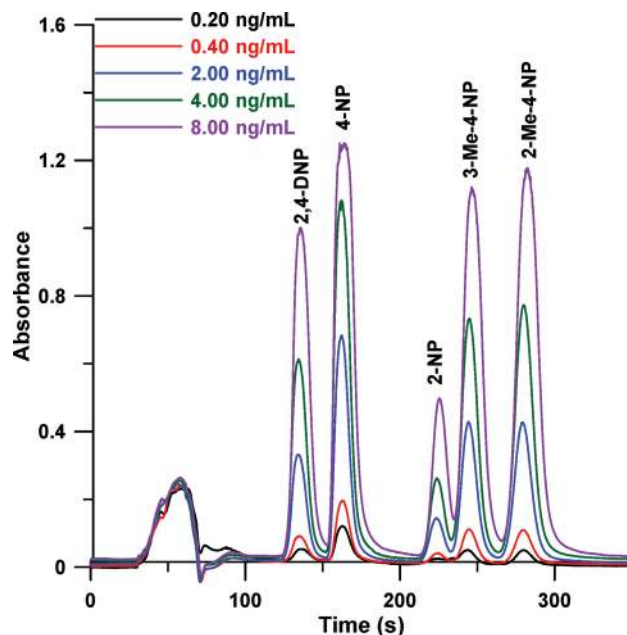within a factor of 4 of the MS/MS instrument and actually does better in one case. The CA-LCW approach may also be applicable to humic-like substances (HULIS) in the atmosphere, of considerable current interest; this class of compounds is also best separated by a two-dimensional strategy.[61]

**Nitrophenols in Rain.** Rainfall in Arlington, TX contained 4-NP as the most abundant NP, in one case close to 5 $\mu$g/L. The concentration data (analysis of 22 samples selected from those over a 15 month period spanning 5/08−9/09) for 4-NP, 2,4-DNP, 2-Me-4-NP, and 2-NP respectively, were (mean ± sd, range): 1.80 ± 1.30, 0.20−4.89; 0.39 ± 0.70, 0.04−3.31; 0.65 ± 0.59, 0−2.26; and 0.35 ± 0.20, 0−0.69 $\mu$g/L. 3-Me-4-NP was detectable in some samples but was below the limit of quantitation (~3× LOD). All samples were analyzed at least in duplicate. The mean variance for replicate analysis of 4-NP, 2,4-DNP, 2-Np and 2-Me-4-NP in individual samples was 2.3, 6.8, 25.0, and 7.3%, increasing with decreasing average analyte concentration.

In the five samples collected over 2/09−3/09 in Houston, 2-NP was undetectable and 2-Me-4 NP (mean ± sd: 0.32 ± 0.24, range: 0.15−0.49 $\mu$g/L) exceeded 2,4-DNP (0.17 ± 0.12, 0.05−0.29 $\mu$g/L). While 4-NP was still the dominant NP (1.03 ± 0.02, 0.82−1.24 $\mu$g/L), 3-Me-4-NP was easily measurable in all samples (0.15 ± 0.07, 0.09−0.22 $\mu$g/L). An illustrative MS/MS chromatogram of a rain sample is shown in Figure S5 in the Supporting Information. Overall, measured NP concentrations in rain were in the same range as those reported in Japan[2] and Europe.[23,33]

**3-Methyl-2-Nitrophenol vs 3-Methyl-4-Nitrophenol.** It is difficult to distinguish between these two isomers by reverse phase separation; MS/MS is not able to easily resolve this either. However, they are readily separated by chiral phases that recognize molecular shapes.[62,63] Such analysis showed that the

(61) Limbeck, A.; Handler, M.; Neuberger, B.; Klatzer, B.; Puxbaum, H. *Anal. Chem.* **2005**, *77*, 7288−7293.
(62) Armstrong, D. W.; Demond, W. *J. Chromatogr. Sci.* **1984**, *22*, 411−415.
(63) Armstrong, D. W.; Demond, W.; Alak, A.; Hinze, W. L.; Riehl, T. E.; Bui, K. H. *Anal. Chem.* **1985**, *57*, 234−237.
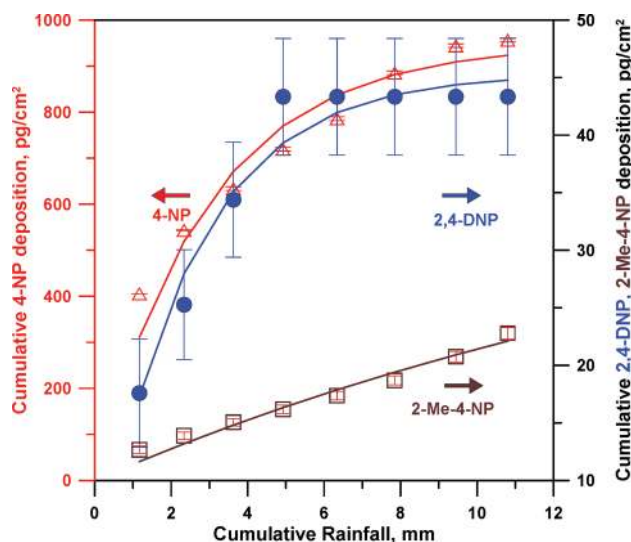
**Figure 5.** Triangles, circles, and squares represent cumulative deposition of 4-NP (left ordinate), 2,4-DNP, and 2-Me-4-NP (right ordinate), respectively, as rainfall continues.

isomer is essentially exclusively 3-Me-4-NP. (See Figures S8–S10 in the Supporting Information.)

**Sequential Rain Samples.** The relatively small sample requirement allows sequential rainfall analysis with good (~1 mm) resolution. The more soluble NPs are rather rapidly washed out from the atmosphere, and the cumulative deposition pattern as a function of rainfall should fit a first order pattern. Figure 5 shows such data for 10−21−2009 for three NPs. 3-Me-4-NP was detectable in all samples but was too low to quantify. The best-fit first order removal rate constants for the washout pattern of 4-NP and 2,4-DNP (the two most soluble NPs: Henry's law constant, $K_H$, $7.7 \times 10^4$ and $1.2 \times 10^4$ M/atm, respectively[17]), are within 20% of each other. In contrast, 2-Me-4-NP exhibited an order of magnitude lower removal rate constant; $K_H$ is not available for this compound but that for the 4-Me-2-NP isomer is 64 M/atm. It appears that sequential rain profiling can be a convenient measure of washout efficiencies of NPs and similar species.

**Air Analysis.** These results are discussed here only briefly because discrete sorbent sampling and off-line elution is not the best way to measure gas phase NPs. Nevertheless, we participated in a field campaign (http://sharp.hnet.uh.edu/doku.php/home) without sufficient time to develop a chromatographically interfaced continuous sampler. Belloli et al.[26] previously found silica gel to be superior to XAD-2 for trapping NPs. We compared XAD-4, XAD-16, and $Na_2CO_3$-impregnated silica gel as well. All XAD-sorbents either had to be precleaned or bought precleaned. NPs trapped on $Na_2CO_3$-impregnated silica gel could not be eluted with water/methanol/acetonitrile without acid addition; this needed neutralization prior to preconcentration. A 60 Å pore size silica gel appeared the best overall choice and was used. In a serial two-cartridge arrangement, the NP was entirely found in the first cartridge (sampling rate: 1 to 2 SLPM, 23−83% RH, and 20−150 μg/m³ of 2-NP or 5-MeO-2-NP).

Initial experiments utilized pure methanol or acetonitrile for elution of a pure NP from the sorbent and were measured by direct spectrometry after adding alkali. It was found, however,
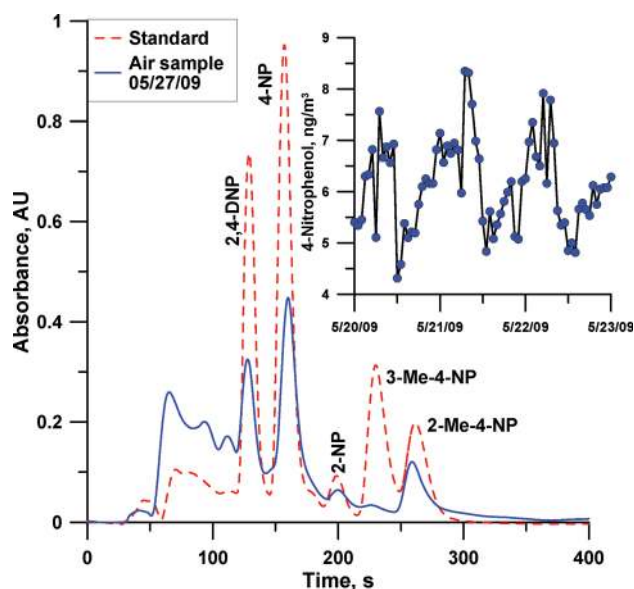


**Figure 6.** Air sample extract chromatogram compared to an aqueous standard containing 2,4-DNP (1 ng/mL), 4-NP (2 ng/mL), 2-NP (1 ng/mL), 3-Me-4-NP (2 ng/mL), and 2-methyl-4-nitrophenol (2-Me-4-NP, 1 ng/mL). The inset shows air concentration data for 4-NP over a 3-day period in Houston, TX; the minima always occurs around noon.

that NPs cannot be concentrated on the AG-21 preconcentrator from pure methanol but 25% methanol was acceptable. We used 50% methanol for elution and diluted 1:1 with water prior to preconcentration. Relevant data are presented in Table S2 in the Supporting Information.

Not surprisingly, the same NPs that we found to be dominant in rain were the dominant NPs in air. Figure 6 shows a chromatogram of an air sample extract compared with an aqueous standard, and the inset shows an illustration of the variation of gaseous 4-NP over a 3-day period. Concentration minima were always observed around the noon hour.

In summary, we have proposed a simple and novel technique that should be readily extendable to multiwavelength measurement and, thus, have broader potential applicability.

## SUPPORTING INFORMATION AVAILABLE

Additional information as noted in text. This material is available free of charge via the Internet at http://pubs.acs.org.