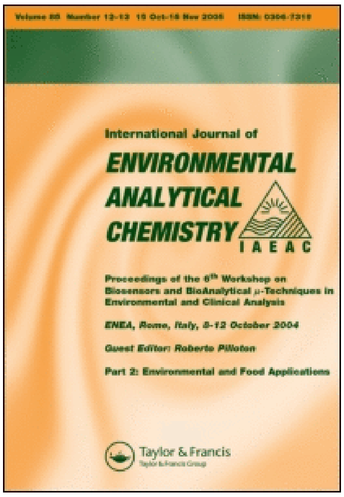

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Leaching of Nutrients and Trace Metals from Aerosol Samples; A Comparison Between A Re-Circulation and an Ultrasound System

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To cite this Article Eyckmans, Kurt , Zhang, Jing , De Hoog, Johan , Joos, Pieter and Van Grieken, René(2001) 'Leaching of Nutrients and Trace Metals from Aerosol Samples; A Comparison Between A Re-Circulation and an Ultrasound System', International Journal of Environmental Analytical Chemistry, 80: 3, 227 — 243

To link to this Article: DOI: 10.1080/03067310108044372

URL: http://dx.doi.org/10.1080/03067310108044372

Intern. J. Environ. Anal. Chem., Vol. 80(3), pp. 227-243
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LEACHING OF NUTRIENTS AND TRACE METALS FROM AEROSOL SAMPLES; A COMPARISON BETWEEN A RE-CIRCULATION AND AN ULTRASOUND SYSTEM

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(Received 15 June 2000; In final form 9 February 2001)

As part of a project investigating the air-water exchange of nutrients and inorganic micropollutants to the North Sea, the atmospheric deposition of nutrients and trace metals in their different compositions and via various pathways was investigated. Intensive sampling campaigns were organised on the research vessel Belgica (ns 21/98 campaign from September 28 to October 1, 1998 and ns 10/99 campaign from April 19 to 23, 1999), at a sampling station near the Belgian coast (Knokke-Heist) and at the University campus of Antwerp. Simulation work and remobilisation experiments were carried out to obtain a general view of the kinetics of solubilisation of the constituents under investigation. Sample treatment requires a leaching system with a quantitative recovery of the species of interest in the leaching solution within a reasonably short period of time (30 min).

For this reason, a re-circulation leaching system was developed, tested, optimised and compared with a more accepted ultrasound leaching method.

Keywords: Leaching; ultrasound; re-circulation; mini-loop; nutrients; trace elements

INTRODUCTION

Previous studies have shown the importance of the atmospheric deposition as a route of a variety of substances, such as nutrients and trace metals, to the terrestrial and aquatic environments [1–7].

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For example the North Sea, in terms of gross nitrogen inputs, the contribution from the atmosphere is relatively minor. The nitrogen input is dominated by the North Atlantic inflow and best estimates suggest that, on an annual basis, the atmospheric input of nitrogen to the North Sea amounts to 40 % of the input of estuaries and 26% of the total terrestrial input. However, the relative importance of the atmospheric input of nitrogen to the southern part of the North Sea is strongly influenced by the nature of the North Sea circulation. The central southern North Sea is somewhat isolated from the influence of the North Atlantic inflow, the English Channel and the river run-off. Furthermore, the importance of the atmospheric influence increases when the seasonal input is considered. The nitrogen inputs from rivers, the North Atlantic and the English Channel are at a minimum during the summer months, whereas the atmospheric input reaches a maximum [2,7]. Therefore, it is possible that during the algae blooms, during late spring and summer, when primary production in the North Sea is often nitrogen limited, the atmosphere may provide the dominant source of nitrogen.

For some trace metals, anthropogenic processes are the most important source to the North Sea atmosphere, and, as far as composition is concerned, the anthropogenic fraction of the North Sea aerosol approximates that of the average anthropogenic European trace metal emissions. There is a south-north decrease in the emission of trace metals to the atmosphere from the land masses surrounding the North Sea. Therefore, the highest concentrations are detected adjacent to the coast, with a fall in concentration towards the north as the air masses become more distant from the sources and the aerosols are depleted by deposition mechanisms. Data indicate that large fractions of the trace metal concentrations in the aerosols are environmentally mobile [1,8–10]. Some of these trace elements such as Al, Si, Mn and Fe are biologically important, while some trace metals, such as Cr, Ni, Cu, Zn, Cd, Hg and Pb are toxic, and may have detrimental effects on the marine ecosystem. For the investigation of the atmospheric deposition of nutrients and trace metals to the North Sea, intensive sampling campaigns have been organised and a sample treatment procedure for aerosols was developed. There have been a number of publications on methods for nutrient and trace metal leaching from aerosols [11–13]. The total concentration of the elements in the atmospheric aerosol particles can indicate the sources of the pollutant, and the chemical speciation can be used to asses the different species in the aerosol sample. Sequential extraction procedures are commonly used to isolate metals associated with the 'water-soluble', the 'acid soluble' and the residual fraction. When the aerosols are mixed with an aqueous solution, the anthropogenic metals are preferentially released; they have the most harmful impact on the biological community.

It was necessary to have a standardised method for sample preparation and analysis, to enable a comparison between data of samples collected on various cruises or different studies. In this study, the extraction and determination of aerosol components which are soluble in water and dilute acids have been investigated.

EXPERIMENTAL

Sampling

Samples were taken during the ns 21/98 and ns 10/99 cruise on the R.V. Belgica from September 28 to October 1, 1998 and from April 19 to 23, 1999, respectively. During the former campaign, a low-volume pumping system Edwards Speedyvac 2 was used (25 l/min) with a 47 mm Nuclepore® filter, pore size 0.4 µm, and a standard filter holder, positioned 12 meters above sea level on a fishing rod. Sampling was carried out over a period of 9 hrs to 16 hrs, collecting 13 m^3 to 24 m^3 of air, respectively. During the ns 10/99 campaign, a high volume pump system was used, a Becker SV 5.130/2 surpressor (30 m^3/h), with a Whatman® GF/B 150 mm filter. The higher background values for trace elements on the Whatman® filter was compensated by the higher collected aerosol masses. An average volume of 360 m^3 of air was sampled over a period of 12 hrs. Samples were changed in the laboratory of the ship under clean bench conditions. The samples were stored at –20°C on the ship. Using the Edwards low-volume pumping system, samples were taken at the UIA campus from July 28 to August 5, 1998. The sampling was on a daily basis, including one sample during day-time (from 9.00 until 21.00) and one during the night (from 21.00 until 9.00). After the samples were taken, they were stored deepfrozen at – 20°C. The sample preparation and manipulation was carried out in the laboratory under a laminar air-flow bench to avoid contamination.

Finally, from June 1999, samples were also taken on a weekly basis at Knokke-Heist, near the Belgian coast, on approximately 500 m from the sea in a rural environment. Sampling was over a period of 24 h, representing an air mass of aproximately 750 m^3. The filters were changed, treated and stored as for the UIA samples.

The re-circulation leaching system

A mini re-circulation system was developed at the laboratory (see Figure 1); it was basically made out of a three-way valve (A), a peristaltic pump (B) with an adjustable flow rate of 0.5 – 3.0 ml/min, a mini-column (ca. 0.4 ml) (C), a teflon filtration set (filter diameter 20 mm) (D), an in-line pH-meter and a purge or tap (E). The re-circulation volume of the mini-loop could be varied from 1.5 ml to 5 ml. The 47 mm Nuclepore® filter is curled up and placed in the mini-column. The 20 mm teflon filter holder was to avoid the presence of undissolved particles in the leached solution. At the start of the leaching procedure, the valves 1 and 3 were opened, and valve 2 was closed. The Milli-Q® water was pumped out of the recipient via 1 and passes through valve 3, the peristaltic pump, the sample filter holder, the teflon filtration set and the pH-meter. In the meanwhile, the purge and valve 1 were closed and valve 2 was opened, so the sample solution could circulate a certain time. When the leaching was accomplished, valve 1 was reopened and valve 2 was closed again. The sample solution could then be collected via E.

The system was also used in a different configuration. When it was used as a linear set-up (valve 1 and 3 open, valve 2 closed and direct storage via E), it gave us the opportunity to follow up the leaching process milliliter per milliliter and to plot concentrations of certain analytes as a function of time or leached volume. The milli-Q water was also acidified so that the solubility as a function of pH could be determined.

The solution was then ready for subsequent analysis with Ion Chromatography (IC), using a Dionex 4000 i equipped with an AS 11-column,

A number of laboratory experiments were carried out to test the application of the re-circulation system in combination with Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES), using a Jobin Yvon 124 unit, for major elements and selected trace metals. The sampling rate was 0.7 ml/min and the integration time 1 s.

The ultrasound leaching system

As already mentioned in literature, ultrasound can be applied in leaching processes [13,14]. The characteristic effects of ultrasound actually arise from the manner in which sound is propagated through the media. Vibration in a liquid generates a series of compressions, creating areas of high and low pressure. When the pressure in the liquid drops below its vapour pressure, cavities are formed. This cavitation is responsible for the hydrodynamic, physical and chemical processes on the surface of the sample. Cavitation is a three step process, consisting of nucleation, growth and collapse of gas or vapour-filled bubbles in a liquid medium. Ultrasonic vibrations cause an increase in the diffusion layer thickness and, thus, an increase in the leaching rate. Comparable leaching rates can be obtained, applying higher temperatures and pressures (hydrothermal treatment) but this has the disadvantage that volatile organic compounds can be lost.

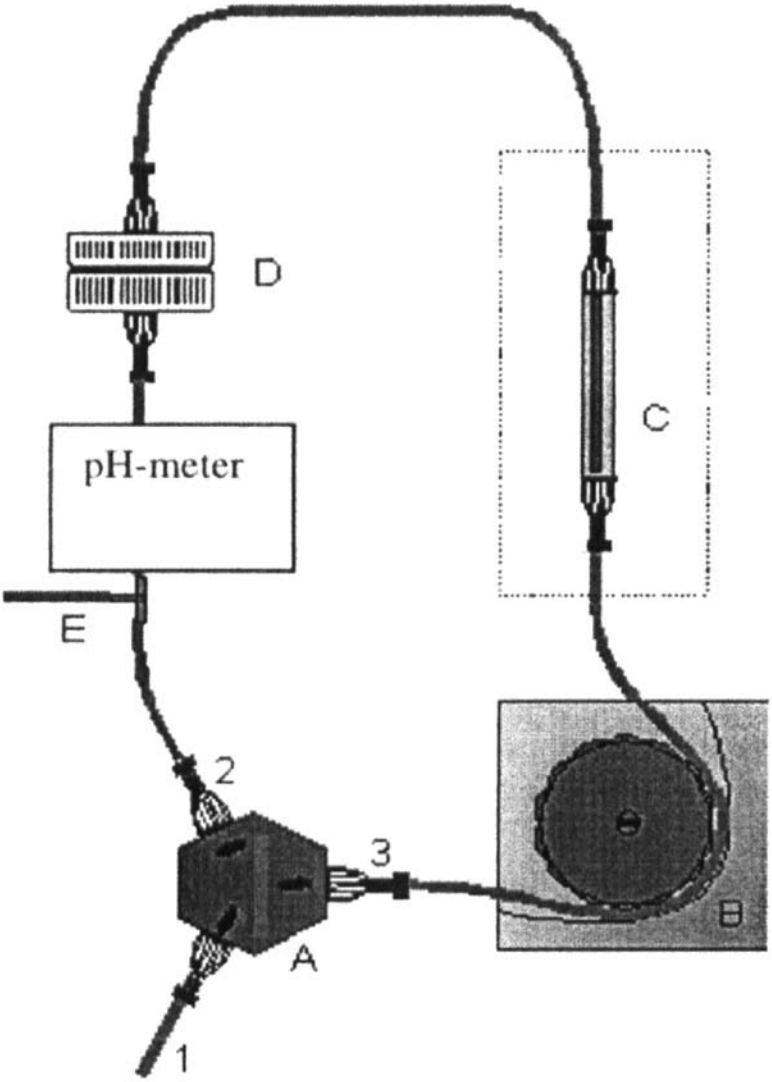


FIGURE 1 Scheme of the mini re-circulation system

For our experiments, a Branson Bransonic 2210 ultrasonic cleaner was used in the laboratory. Pieces of filters with a diameter of 20 mm were punched out of a 150 mm Whatman GF/F filter and placed in a plastic sample vessel. Three ml of Milli-Q water was added and the vessel was placed in the ultrasound system for 20 min.

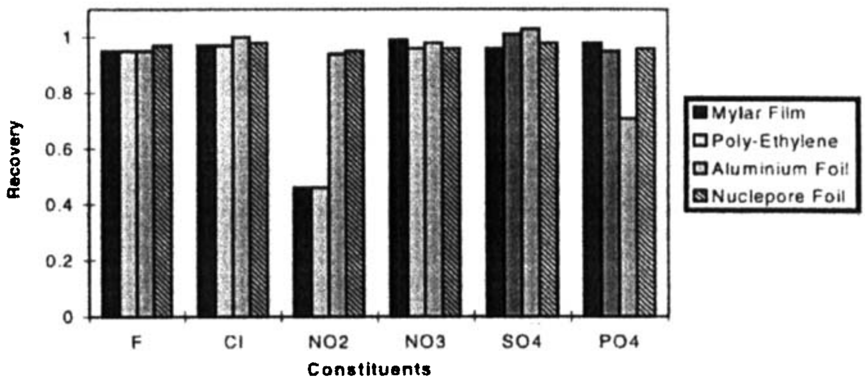
RESULTS AND DISCUSSION

Optimisation of the re-circulation system

A number of factors, which affect the recovery of the nutrients from the aerosol samples and the precision and detection limit of the final analysis, were optimised with IC. As standard aerosol samples with certified nutrient concentrations were not commercially available, standard samples were made in the laboratory with salt solutions. The anions under investigation were: F^-, Cl^-, NO_2^-, NO_3^-, SO_4^{2-} and PO_4^{3-}.

Recovery

A series of standard samples with spiked species of interest was prepared in the laboratory. A Mylar Window Film (MF), a Nuclepore filter (NF), a piece of low density poly-ethylene (PE), and a piece of aluminium foil (AF) were used and the recoveries from the different substrates compared (Figure 2). Glass fibre filters were not used for the optimisation since these filters had a high dead volume due to absorption of the liquid. NO_2^- showed a low recovery (20–40%) when the standard solution was spiked on the Mylar Foil and on the Nuclepore filter. Higher recoveries could be obtained when the standard solution was spiked on the aluminium foil. However, using this substrate, the recovery of PO_4^{3-} was considerably reduced (by 30%). When the Nuclepore filter was used, an overall recovery of 90–110% was reached for the species of interest.



Artificial Samples

FIGURE 2 Recoveries from the different substrates

Flow rate

An aerosol sample from 20 m^3 of air on a 47 mm Nuclepore filter was used as a test sample. When the flow rate of the system increased from 0.9 ml/min to 1.7 ml/min, the time of the maximum extraction for Cl^-, PO_4^{3-}, SO_4^{2-} and F^- nearly halved (Figure 3). Using the maximum flow rate of the system (3 ml/min), an optimal extraction time of 30 minutes was obtained for the sample extraction with Milli-Q water. A disadvantage of this higher flow rate was a decreasing reliability of the system. With the higher pump speed, the pressure within the system increased and leakage of the leaching solution out of the re-curculation system could occurre. Due to the mini-column and the mini filter holder, which caused pressure differences in the loop, also some air leakage into the system could happen, causing a disturbance of the flow. Sometimes, by increasing the pump speed, also the filter could collapse in the mini-column en could block the flow, resulting in an increase of the pressure and leakage of the sample solution.

Number of extractions

The results showed that the extraction with 2 ml of Milli-Q water could recover 75% of major species. Since no commercial aerosol standards were available, and given the asymptotic behaviour of the concentrations as a function of the number of extractions, a double extraction with 1 ml of Milli-Q water for samples from an air volume of 5 to 10 m^3, or a double extraction with 2 ml of Milli-Q water for samples from an air volume of 20–30 m^3 seemed to be appropriate for the sample analysis using a maximum flow rate.

Experiments and results of the re-circulation system with IC

For the daily-based samples, taken at the UIA campus, 47 mm Nuclepore filters were used. These samples were used to examine the difference in aerosol composition between day-time and night-time, and to investigate daily variations in the aerosol compositions. The results are depicted in Figures 4a-e. A significant difference between day-time and night-time concentrations of the species of interest can be observed, which possibly reflects the influence of traffic or other anthropogenic sources.

The concentration on air-volume base (µg/m^3) are sometimes five to ten times higher during the day than during the night. Several sources and/or mechanisms can be responsible for this observation. Sulphate shows higher levels during day time, while on the other hand, nitrate shows often higher night-time concentrations. During night time, the nitrate radical, NO_3, formed by the reaction of NO_2

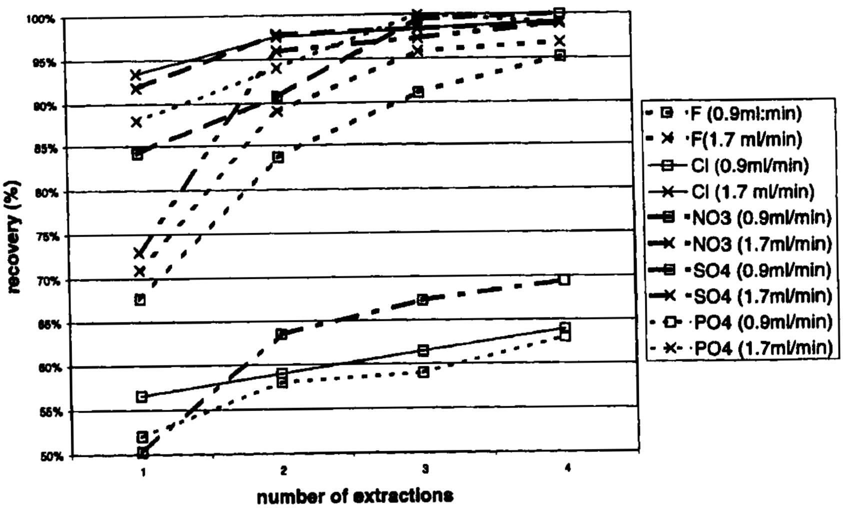


FIGURE 3 Recovery as a function of number of extractions and flow rate

with ozone (O_3), becomes more significant. NO_3 reacts with NO_2 to form nitrogen pentoxide (N_2O_5) which is subsequently hydrolysed to form HNO_3.

The daily variation of the aerosol concentration is also significant; the daily concentrations may differ by a factor of five. Concentrations of nitrate and sulphate are in general higher than that for chlorine, indicating that a substantial amount of nitrate and sulphate was accumulated in the air and/or chlorine in the aerosol was replaced by other species, resulting in a nitrate/chlorine and sulphate/chlorine ratio of 3 or even higher [15,16].

Experiments and results of the re-circulation system with ICP-AES

The determined analytes were Na, Cu, Fe, Pb, Al and Ca. Sodium was used as a seasalt index, Ca is originating from soil and seasalt particles ($CaCO_3$, $CaSO_4$,).

Aluminium and Fe have a crust dominated contribution and imply to a lesser extent fly ash. Cu and Pb are anthropogenic pollutants.

For these analytes the following aerosol samples were used (see Table I). Samples were collected indoors in the laboratory of the UIA campus, outdoors at the UIA campus and over the North Sea during the Belgica 21/98 cruise.

In each series, two samples within the same category were combined. The leaching system was used in the linear set-up.

TABLE I List of used samples. Eyckmans Kurt, Department of Chemistry, University of Antwerp, Universiteitsplein 1, B-2610 Wilrijk, Antwerpen

Category	*Date*	*Air Volume* (m^3)	*Series#*	*Leaching flow*
Indoor	12/01/99	27.1	2	0.5 ml/min
	21/01/99	32.8		
Outdoor	22/01/99	15.7	3	0.5 ml/min
	23/01/99	15.9		
North Sea	28/09/98	23.9	4	0.5 ml/min
	29/09/98	13.0		
Indoor	11/01/99	19.2	1	1.9 ml/min
	14/01/99	28.5		

In the first experiment, the leaching flow rate was fixed at 0.5 ml/min. The leaching was processed initially with Milli-Q water (i.e. pH=5.60) and the pH of the Milli-Q water was then reduced [7,8] to pH=2.20 by adding HCl 37% after 24 min (i.e. after 12 ml) (Figures 5a-f). For each series, 20 samples of 1 ml were collected

Sodium is immediately soluble in Milli-Q water at pH=5.6 for all three kinds of aerosol samples, indicating the environmental mobility. This is probably due to the dominance of seasalt for this element in aerosols from both North Sea and more continental stations (Figure 5a). A second but less significant peak of Na was found at pH=2.50 for indoor aerosols, which suggests that some of Na from indoor aerosols is combined with particles that are not soluble in Milli-Q water.

In Figure 5b the kinetics for the dissolution of Al is shown. A clear bi-peak model, representing the dissolution of the Al compounds at neutral pH (Milli-Q water) and the dissolution in the acidified leaching solution can be observed. For both outdoor and North Sea samples, a sharp and prominent dissolution of Al takes place at pH=5.6 in Milli-Q water, followed by a less important but more smooth release of this element at lower pH value (pH=2.20). The indoor aerosol samples illustrate an opposite solubility pattern with a fivefold higher concentration at pH=2.20 than at pH=5.60.

The different dissolution behaviour suggest a different sample composition for the Al compounds on the outdoor and indoor samples. Where the outdoor samples contain a higher Al compound fraction that dissolves at neutral pH, the highest fraction of the Al compounds on the indoor samples are dissolved at lower pH.

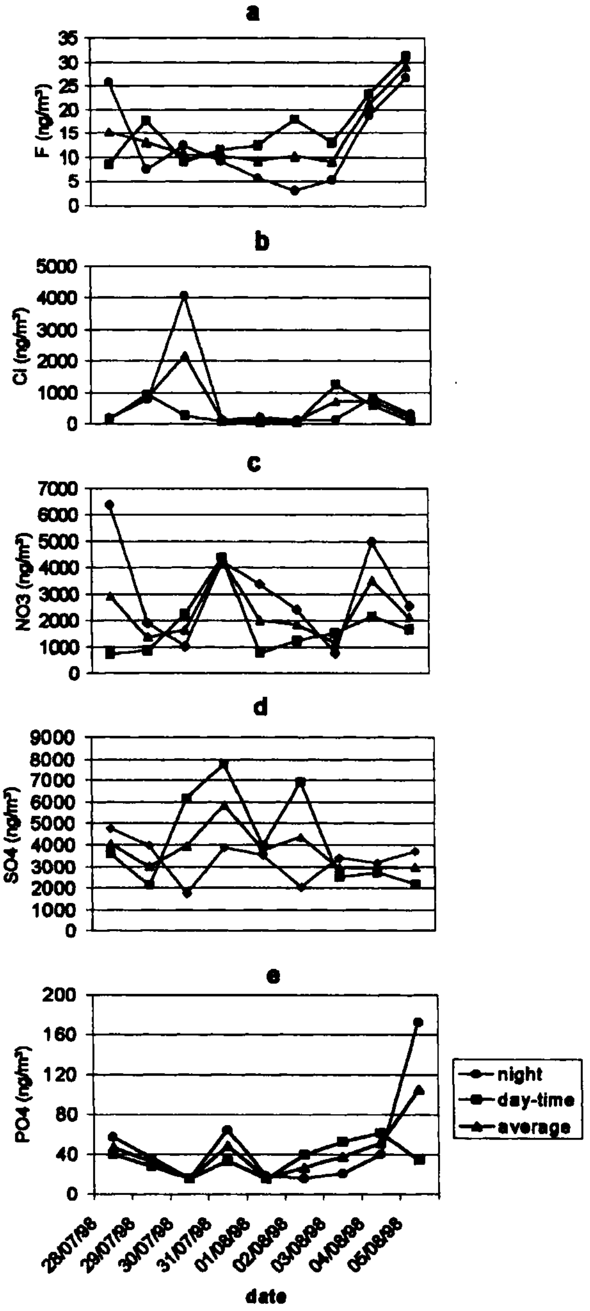


FIGURE 4 a-e: Day-night and daily variations for the different ions, (C in ng/m^3)

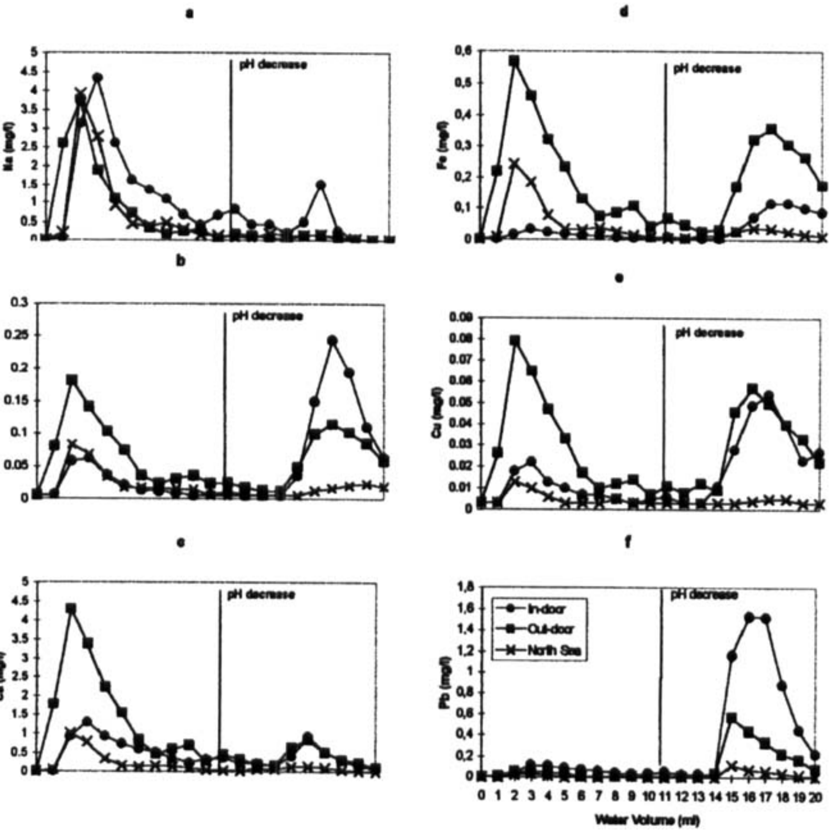


FIGURE 5 a-f: Leaching of the different elements at a different pH

Calcium has a dominant soluble fraction in Milli-Q water at neutral pH (pH=5.60), followed by a rather significant increase at lower pH (Figure 5c). This indicates that apart from seasalt, which is the dominant source of Ca-aerosol, a significant amount of Ca exists as soil particles (e.g. calcite or gypsum) indoors as well as outdoors. For the samples from the North Sea, however, Ca is probably dominated by the seasalt fraction in aerosols, which can be seen from the solubility pattern (Figure 5c).

Fe shows a similar distribution as Al when the concentration is plotted against the leaching volume (Figure 5d). A significant increase in concentration at pH=2.20 may suggest that some of the Fe-oxides are remobilized, most significantly for indoor aerosol samples. The samples collected from the North Sea illustrate a predominant dissolution at pH=5.60, followed by a lower and slow remobilization when the pH is further reduced.

Cu and Pb had very different behaviours in these experiments (Figures 5e and 5f). Cu has a similar bi-peak pattern as Al in the leaching experiment, whereas Fe and Pb did not show any enhanced solubility at pH 5.6. Solubility could only be attained under acidic conditions (pH 2.2). This pattern was observed for both inland and North Sea samples.

In a second experiment, the leaching flow rate for the indoor aerosol samples was increased to 1.9 ml/min, under the same conditions. Each sample contained 1.5 ml of leaching solution, compared to 1.0 ml at a leaching rate of 0.5 ml/min. The data obtained were compared with those from the previous experiment with a lower flow rate (i.e. 0.5 ml/min) (Figure 6).

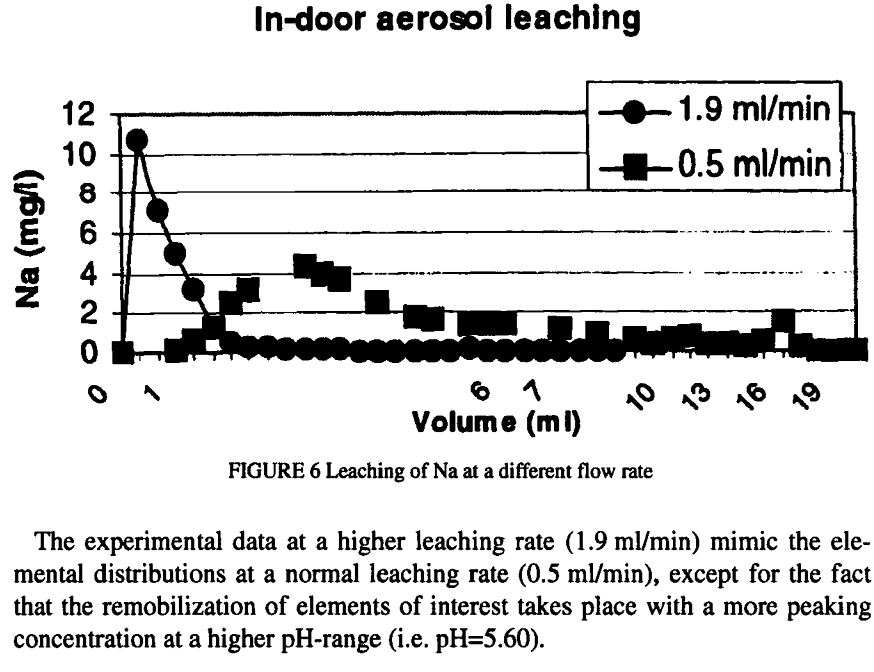


FIGURE 6 Leaching of Na at a different flow rate

The experimental data at a higher leaching rate (1.9 ml/min) mimic the elemental distributions at a normal leaching rate (0.5 ml/min), except for the fact that the remobilization of elements of interest takes place with a more peaking concentration at a higher pH-range (i.e. pH=5.60).

Optimisation of the ultrasound system with IC

As for the re-circulation system, the ultrasound system was optimised using an aerosol sample prepared by the evaporation of a mixed salt solution on the filters (spiking). Nuclepore filters with a diameter of 20 mm were used. Extraction time and volume were optimised and the recovery was checked.

The Nuclepore filter was placed in a plastic sample vessel, three milliliters of water were added and placed for ten minutes in an ultrasonic bath. The solution was filtered using a Millipore MILLEX®-GV 0.22 µm pore size filter unit and the solution was ready for IC or ICP-AES analysis.

In Figure 7, the recovery as a function of the extraction time is given. More than 80 % of the soluble fraction is remobilised in the solution after 5 min, with an entire remobilisation after 20 min. This recovery was measured in 3 ml of Milli-Q water. In Figure 8 the recovery per ion after a leaching time of 20 minutes is demonstrated.

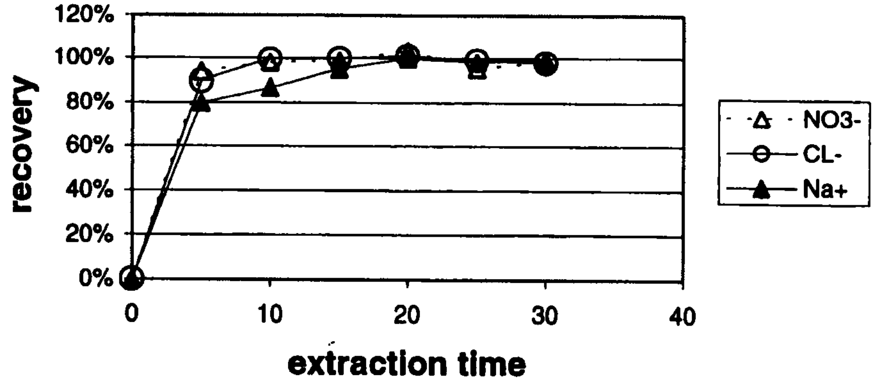


FIGURE 7 Recovery as a function of extraction time

Samples for the high volume pump system were taken on Whatman GF/B 150 mm filters during the ns 10/99 campaign. Small pieces of filters (47 mm and 20 mm diameter) were punched out of the 150 mm filter and analysed with IC. The concentration of the pollutants in the air was calculated out of the concentrations of the analysed leaching solutions.

Experiments and results of the ultrasound system with ICP-AES

A 150 mm Whatmann GF-B sample was taken at the Belgian coast on 29/11/99. Eleven pieces were punched out of the filter and were leached with 11 solutions of different pH. They were all placed in the ultrasound bath for 20 min and analysed with ICP-AES. For the same reasons as stated in section IV. 3, we analysed the samples for Na, Cu, Fe, Pb, Al and Ca.

The pH was changed from 6.6 to nearly 2, and different solubility patterns can be seen for most of the elements. For Al and Fe (Figure 9a), we have a continuous increase in solubility when the pH was decreased below pH 4. The solubility of Pb is higher under low pH conditions. In Figure 9b, we can see that almost all the Na and Ca is dissolved at a neutral pH.

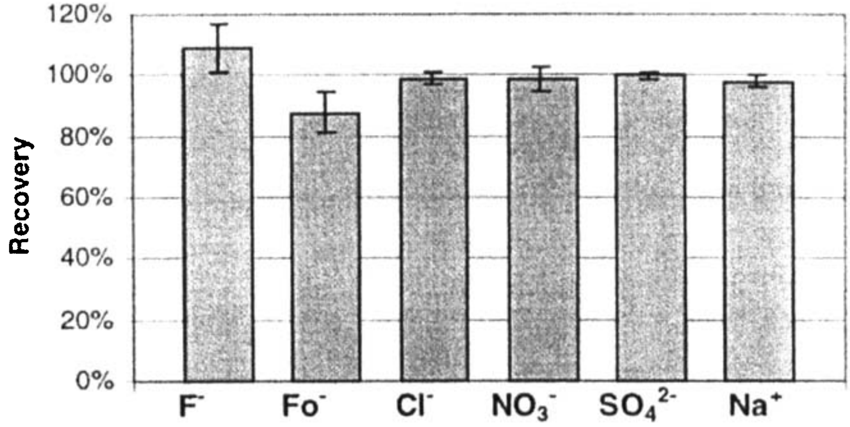


FIGURE 8 Recovery for each ion (20 min.)

Comparison between the re-circulation system and the ultrasound system

The samples of the ns10/99 campaign were used to compare the two leaching systems. The small punched filters were analysed with IC. In Table II, the results are given for a sample, taken at the Southern bight of the North Sea on 20/4/99 and it represents an air mass of 351.5 m^3.

TABLE II Comparison between the re-circulation system and the ultrasound system Eyckmans Kurt, Department of Chemistry, University of Antwerp, Universiteitsplein 1, B-2610 Wilrijk, Antwerpen

Element	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}	F^-	Cl^-	NO_2^-	NO_3^-	SO_4^{2-}
Mini-loop	3.57	1.67	0.506	0.261	0.360	0.104	2.08	0.0868	5.56	2.49
Ultrasone	3.82	4.44	1.18	0.230	0.398	0.131	4.85	0.0271	13.8	8.10

A remarkable difference for certain ion concentrations, like ammonium-, nitrate- and sulphate, was observed. Some values, however, seem to be very comparable, this especially for the easily-soluble Na-, Mg- and Ca-salts. The mini-loop system consequently gives a lower concentration for most of the other elements. This is probably due to the fact that these ions in the aerosols are not as easily soluble as the spiked salt solutions on the filter. For the real aerosol components, the mini loop system is necessary to solve the soluble aerosol fraction. This observation is also in agreement with data found in literature [14]. In all the experiments, the mini-loop system gave a lower concentration for most of the other elements.

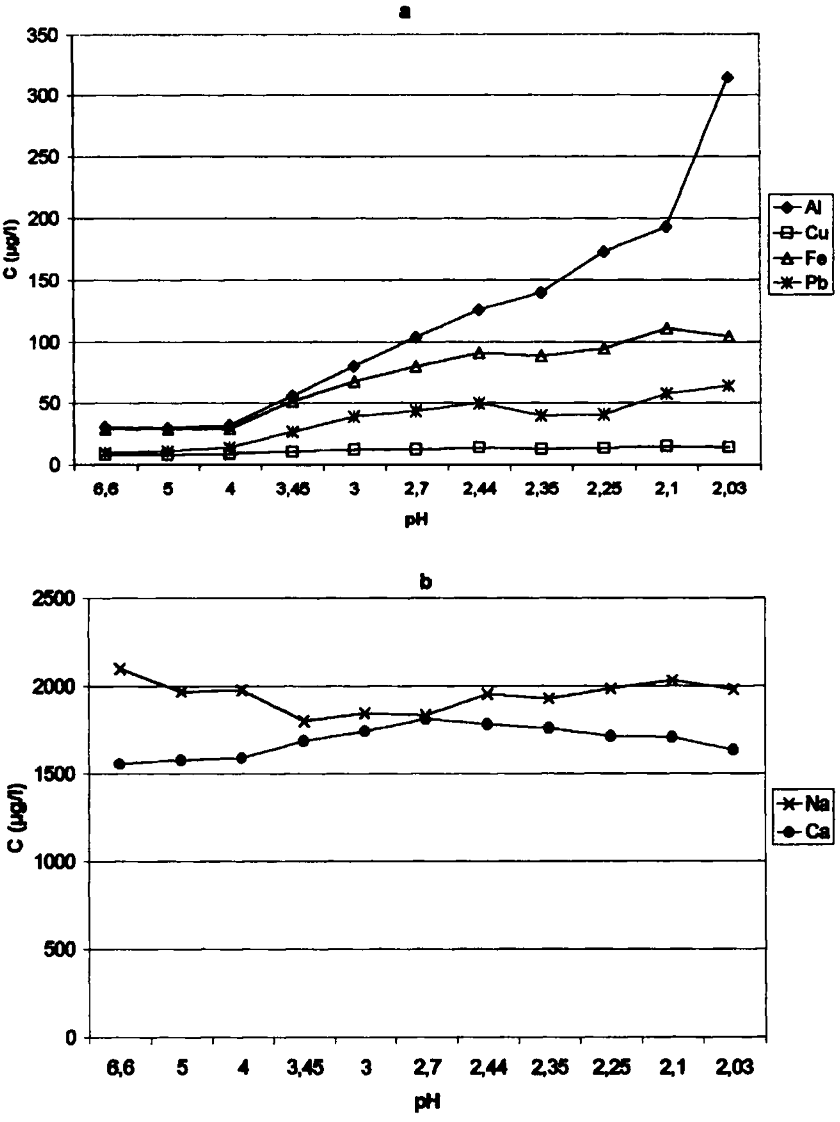


FIGURE 9 a-b: Solubility of trace elements as a function of pH

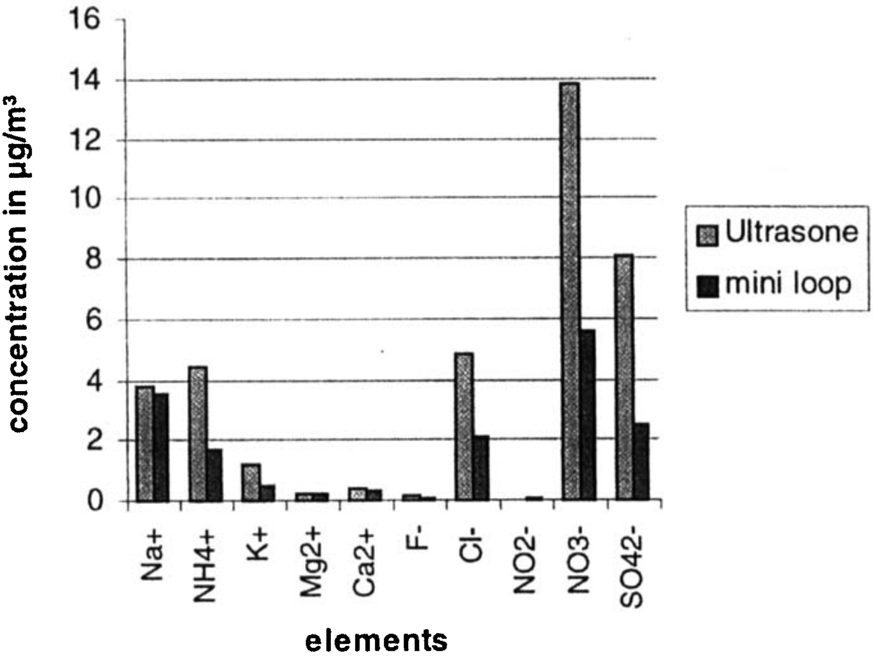


FIGURE 10 Comparison between the re-circulaton system and the ultrasound system

CONCLUSIONS

When comparing the two methods, the recoveries on aerosol samples with the re-circulation method appeared to be insufficient. Especially the ion concentrations of the less soluble aerosol salts were much too low.

Also, during the use of the mini-loop system, leaking of the sample solution often occured and samples were lost due to these practical problems. Even when the system worked properly, the labour-intensivity of the mini-loop system was much higher than when using the ultrasonic method.

On the other hand, the mini-loop system offered the possibility to monitor the leaching process easily as a function of time, leaching volume and pH.

Acknowledgements

This work was financed by the Belgian State, the Prime Minister's Office for Services for Scientific, Technical and Cultural Affairs (Contract MM/DD/10).

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