Published in final edited form as:

Environ Sci Technol. 2012 December 4; 46(23): 12806–12813. doi:10.1021/es3019572.

Heterogeneous Atmospheric Chemistry of Lead Oxide Particles with Nitrogen Dioxide Increases Lead Solubility: Environmental and Health Implications

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Abstract

Heterogeneous chemistry of nitrogen dioxide with lead-containing particles is investigated to better understand lead metal mobilization in the environment. In particular, PbO particles, a model lead-containing compound due to its wide spread presence as a component of lead paint and as naturally occurring minerals, massicot and litharge, are exposed to nitrogen dioxide at different relative humidity. X-ray photoelectron spectroscopy (XPS) shows that upon exposure to nitrogen dioxide the surface of PbO particles react to form adsorbed nitrates and lead nitrate thin films with the extent of formation of nitrate relative humidity dependent. Surface adsorbed nitrate increases the amount of dissolved lead. These reacted particles are found to have an increase in the amount of lead that dissolves in aqueous suspensions at circumneutral pH compared to unreacted particles. These results point to the potential importance and impact that heterogeneous chemistry with trace atmospheric gases can have on increasing solubility and therefore the mobilization of heavy metals, such as lead, in the environment. This study also show that surface intermediates, such as adsorbed nitrates, that form can yield higher concentrations of lead in water systems. In the environment, these water systems can include drinking water, ground water, estuaries and lakes.

Introduction

Heavy metals are a major health threat to humans at increased concentrations in the blood stream.¹ Those of highest concern include As, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, Sn, and Tl, whose emissions are regulated. Some of these elements are carcinogenic or toxic, affecting, among other areas, the central nervous system (Hg, Pb, As), the kidneys or liver (Hg, Pb, Cd, Cu), skin, bones, or teeth (Ni, Cd, Cu, Cr).² Emissions of heavy metals into the environment occur *via* a wide range of processes and pathways, including in air (*e.g.* during combustion, extraction and processing), in surface waters (*via* runoff and releases from storage and transport) and in soil (*hence* into groundwater and crops).¹ Thus, there is the potential for humans to be exposed to these harmful agents in air, water, soil and/or food.

Lead is one of the most toxic metals still present in environment. Until 1990, emissions of heavy metals, including lead, increased dramatically from mine production and anthropogenic emissions and became one of the biggest environmental and occupational concerns.³ However, over the last few decades, lead emissions in developed countries decreased mainly due to the use of the unleaded gas.¹ But in spite of an increase in use of

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Supporting Information. Additional XPS data are provided in supporting information. In particular, the valence band spectra are shown and discussed for PbO and NO₂ exposed PbO in Figure S1. This material is available free of charge via the Internet at <http://pubs.acs.org>.

unleaded gas, lead persists in everyday use maintaining its presence and potential for toxic exposure due to legacy sites and its widespread commercial use in batteries, metal alloys, solder, glass and ceramics.⁴ In fact it has been recently suggested that natural disasters, such as Hurricane Katrina, can potentially result in increasing toxic lead levels in residential soil and dust presumably due to the immobilization of lead from older (before 1950s) homes.⁵⁻⁷ Besides stationary sources, exposures to metal-containing aerosols including those that contain lead are feasible as well.⁸⁻¹¹ These aerosols can enter the soil and be absorbed by vegetables, or alternatively be deposited on leaves. Two primary means of environmental heavy metal mobility are atmospheric transport and leaching.¹²

Our interest is related to natural and anthropogenic lead mobilization from stationary sources or airborne sources through atmospheric processing (TOC graphic). Lead in stationary sources, including lead paint, pipes and lead-containing minerals, are often exposed to trace atmospheric gases. The behavior of these elements during atmospheric transport and processing depends on their physicochemical properties, particle size distribution and meteorological conditions. Trace elements associated with atmospheric aerosols can either undergo wet or dry deposition into terrestrial or aquatic environments. While in the atmosphere, atmospheric aerosols can undergo a variety of chemical and physical transformations. A very strong relationship exists between, for example, acid rain and heavy metal concentration with insoluble heavy metals associated with acidic precipitation and accumulation in soil.^{13, 14} This is also related to the presence of gas-phase NO_2 and SO_2 , mainly from anthropogenic emissions from coal-fired power plants.¹⁵

Typical concentrations of NO_2 in the atmosphere found over the urban areas range anywhere from 0 to 25 ppb.^{16, 17} A recent study showed that when exposed to nitrogen dioxide (NO_2) and ozone (O_3), lead-based paint granules became more available for subsequent transfer due to the reaction of these gases with polymeric binders in paint.¹⁸ This may cause great risk of lead poisoning, particularly in rural areas where lead-based paints remain in older buildings and machinery. Although these results were specific to lead, similar processes can occur with other heavy metals. In fact, metal finishing and surface treatment operations in automobile parts, steel strip mills, pole hardware and heavy steel industries have also been shown to emit toxic heavy metal pollutants.¹⁹ Thus reactions of atmospheric gases with heavy metal surfaces need to be investigated to provide a greater detail on possible increase in heavy metal mobility in rural and urban environments.

In this study, PbO , a model compound used in paints that also occurs as the minerals massicot and litharge is exposed to nitrogen dioxide, a common pollutant in air with expected increasing concentrations in the next two decades²⁰ yielding steady increases of nitrate aerosols in the near future.²¹ Following nitrogen dioxide exposures at different relative humidity, the amount of lead that dissolves in aqueous suspensions at pH 7 is measured. These results show that the dissolution of lead increases by as much as threefold following exposure to nitrogen dioxide. X-ray photoelectron spectroscopy shows that surface adsorbed nitrates form following the reaction with nitrogen dioxidewhich leads to the increase in solubility. The environmental and health implications of this study are discussed. To the best of our knowledge, this is the first molecular-level mechanistic study of the reactivity of lead-containing particles with gas-phase NO_2 as a function of relative humidity and the impact this chemistry has on lead dissolution.

Materials and Methods

Materials

Lead oxide, PbO (>99.9%), and lead nitrate, $\text{Pb}(\text{NO}_3)_2$ (ACS grade), particles were purchased from Acros Organics. All particles were used as received. Nitrogen dioxide (NO_2 ,

research grade) was purchased from Matheson and used as received. For relative humidity studies, distilled water (Optima grade from Fisher Scientific) was used. Prior to use, the distilled water was degassed several times with consecutive freeze-pump-thaw cycles.

Particle characterization

Powder X-ray diffraction was performed using Rigaku MiniFlex II with a filtered cobalt source. SEM images were obtained using Hitachi S3400 with 20 kV accelerating voltage operating in variable pressure mode. BET surface areas were determined using a NOVA 4200e (Quantachrome instruments).

Dissolution measurements

Lead dissolution experiments were performed in a glass reactor at room temperature. First, ex situ heterogeneous PbO and NO₂ reaction was performed in an overnight evacuated cell with (a) 100 mTorr NO₂ and (b) 100 mTorr NO₂ and 8 Torr H₂O present to evaluate the effect of NO₂ and relative humidity on a possible mobilization of lead. Samples were then transferred into a solution reaction vessel described before.²² Reacted particles were suspended in Mill-Q water (pH of 6) at a mass loading of 50 g L⁻¹. The suspension was stirred for 24 hours. Aliquot from the supernatant was then passed through a 0.2 μm PTFE filter to remove particles. The concentration of lead ions was measured using Varian 720-ES inductively coupled plasma-optical emission spectrometer (ICP-OES). Dissolution of unreacted PbO was also conducted under the same conditions for comparison. All experiments were conducted in triplicate and result represents the average and standard deviation.

Surface analysis

The experimental setup for reactions and analysis has been described in detail before.^{23, 24} A custom-designed Kratos Axis Ultra X-ray photoelectron spectroscopy system was used. The system contains three chambers, a (i) an ultra high vacuum (UHV) surface analysis chamber; (ii) a sample transfer antechamber and; (iii) a reaction chamber. The transfer antechamber is connected to both the analysis and reaction chamber. Powdered samples were pressed into indium foil and mounted onto a copper stub. In a typical experiment, lead oxide particle surfaces were first analyzed in the surface analysis chamber and then transferred to the reaction chamber where they were exposed to gas-phase reactants in the reaction chamber in the following order: (1) NO₂ and (2) NO₂ and H₂O vapor at various relative humidities, introducing NO₂ first followed by H₂O vapor. Thus, all the reaction experiments were performed consecutively, using the same sample. The time necessary for the introduction of each reactant was approximately 15 seconds. The resulting gas mixture was allowed to equilibrate with the sample for 30 min.

The surface analysis chamber is equipped with monochromatic radiation at 1486.6 eV from an aluminum K_α source using a 500 mm Rowland circle silicon single crystal monochromator. Survey scans were collected using the following instrument parameters: energy scan range of 1200 to -5 eV; pass energy of 160 eV; step size of 1 eV; dwell time of 200 ms and an X-ray spot size of 700 × 300 μm. High resolution spectra were acquired in one sweep of all regions of interest using the following experimental parameters: 20 to 40 eV energy window; pass energy of 20 eV; step size of 0.1 eV and dwell time of 1000 ms. All spectra were calibrated using C1s peak at 285.0 eV. A Shirley-type background was subtracted from each spectrum to account for inelastically scattered electrons that contribute to the broad background. CasaXPS software was used to process the XPS data.²⁵ Transmission corrected relative sensitivity factor (RSF) values from the Kratos library were used for elemental quantification.

Results and Discussion

Sample characterization

First, a detailed physicochemical characterization of PbO particles was performed to better understand the nature of the bulk and surface properties of these particles. Figure 1 shows an SEM image and the XRD pattern of PbO particles. The image shows that the PbO particles have platelet morphology with an approximate particle size of $\sim 5 \mu\text{m}$ for PbO. The large particle size agrees well with the low BET surface area of $0.4 \div 0.2 \text{ m}^2/\text{g}$ measured for this sample. Low surface area lead oxide materials are typical in commercial lead oxide samples.^{26, 27}

The XRD for several lead containing reference compounds and minerals including such as PbO (massicot),²⁸ Pb metal,²⁹ PbO (litharge),³⁰ PbO₂ (plattnerite),³¹ Pb₃O₄ (minium),³² PbCO₃ (cerussite)³³ and Pb₃(CO₃)₂(OH)₂ (hydrocerussite)³⁴ are also provided. It can be seen that orthorhombic PbO in the form of the mineral massicot, was the major constituent as determined from XRD (Figure 1).²⁸ Small amounts of other crystalline phases were also detected in XRD. This is due to the fact that many crystalline lead oxide phases have similar thermodynamical stabilities at ambient pressure and temperature. For example, enthalpies of formation for PbO, massicot and litharge, are -217.3 kJ/mol and -219.0 kJ/mol , respectively, whereas for PbO₂ it is -277.4 kJ/mol .³⁵ Pb₃O₄ has the highest enthalpy of formation of -718.4 kJ/mol and for PbCO₃ it is -699.1 kJ/mol .³⁵ Pb(OH)₂ has been reported to have an enthalpy of formation of -576 kJ/mol .³⁶

It is very feasible that in moist environments, complex surface layers will be formed on PbO particles. In fact, cerussite (PbCO₃), hydrocerussite (Pb₃(CO₃)₂(OH)₂), massicot (PbO) and elemental lead were detected via XRD analysis of the weather materials of lead bullets collected in the shooting ranges.^{37–39} In fact reflections in the XRD pattern shown in Figure 1 at 33 and 37 degrees are due to the tetragonal form of PbO, litharge³⁰ and others at 30, 31, 46 and 82 are due to more complex phases including cerussite (PbCO₃) and hydrocerussite (Pb₃(CO₃)₂(OH)₂). This variety in speciation is in agreement with a wide range of lead compounds detected in urban home dust particles, such as lead citrate, cerussite, lead metal, hydrocerussite and massicot,^{40, 41} as well as other lead salt compounds as detected over Mexico City with elevated concentrations in the early morning due to urban pollution.⁴² From these data and literature studies, it is clear that lead oxides can form carbonate or hydroxide layers in the atmosphere. In fact, PbCO₃ was reported as a final product obtained via contact of PbSO₄ and CaCO₃ particles in aqueous solutions^{43, 44} or via deliquescence induced reactions⁴⁵. As discussed below, XPS analysis before and after reaction with nitrogen dioxide can provide further information about the role of carbonate and hydroxyl layers on PbO samples investigated here.

XPS analysis of PbO particles before and after exposure to NO₂ at different relative humidity

XPS analysis of unreacted, as well as NO₂ reacted PbO particles was performed to detect and quantify species, native to the PbO surfaces as well as products formed following reactions. First low resolution survey scans were acquired of as received PbO particles, as well as those following exposure to NO₂ (100 mTorr) for 30 min. These data are shown in Figure 2. It can be seen that there are several peaks in the XPS. Peaks due to Pb4f, C1s, Pb4d, O1s, Pb4p, Pb4s and O KLL photoelectrons are seen at 137, 285, 411, 530, 641, 892 and 971 eV, respectively. For NO₂-exposed PbO particles, there is a low intensity peak appeared at around 400 eV due to the N1s photoelectrons adsorbed nitrogen species showing that an adsorbed reactive product is formed. As a next step, detailed speciation information can be determined from higher resolution XPS scans in the different binding energy regions.

High resolution XPS data for the each of the O1s, N1s, C1s and Pb4f regions are shown in Figure 3 with the corresponding binding energy values and their assignment tabulated in Table 1. Spectra are shown for as received PbO, reacted consecutively with NO₂ (100 mTorr) under dry conditions <1% RH and NO₂ (100 mTorr) at 1.9, 8 and 18 Torr H₂O for 30 min, corresponding to 9, 38 and 85 % RH. It is also important to evaluate the reference compound for XPS since metal oxides are known to form nitrates on the surface via NO₂ adsorption²³ and spectral peak positions can be established with reference compounds. Therefore, XPS data for Pb(NO₃)₂ in the relevant binding energy regions are also shown in Figure 3.

The O1s region shows primary peak at 528.9 eV for unreacted PbO particles due to lead-oxygen bonds.⁴⁶ An additional peak at 531.1 eV is due to surface hydroxyl groups and/or carbonates.^{47, 48} After reaction with NO₂, the 528.9 peak shifted to 529.6 eV in conjunction with the shift observed in Pb4f region (*vide infra*). This shift O1s shift shows a distinct effect of the adsorbed NO₂ product on the electronic structure of PbO. Shift towards higher binding energies can be related to the high electronegativity of nitrate formed and the extent of the reaction, thus affecting the electronic structure of PbO at the surface. A new peak appears at 533.2 eV due to the oxygen atoms in surface nitrate, Pb(NO₃)₂, in agreement with the O1s binding energy found in the reference lead nitrate spectrum. Finally, when sample was further reacted with NO₂ in a series of increasing %RH, peaks due to surface Pb-O bonds at 529.6 eV almost completely disappear showing O1s due to the formation of Pb(NO₃)₂ (533.2 eV) with a very small amount of adsorbed hydroxyls/carbonates (531.8 eV). Interestingly, these data suggest that within the XPS probe depth of around ~3 nm, the near surface region completely reacts and converts into Pb(NO₃)₂ via heterogeneous reaction with NO₂ in the presence of adsorbed water which is seen to enhance the extent of reaction except for at the highest relative humidity.

The N1s binding energy region shows the formation of surface nitrate from reaction of NO₂ as indicated by the 407.4 eV peak in agreement with the nitrate N1s peak of the Pb(NO₃)₂. This surface nitrate species can be formed in a two-step reaction mechanism via NO₂ adsorption on surface sites followed by recombination into adsorbed nitrate and gaseous NO⁴⁹ (where =Pb represent surface Pb site)

This partitioning has previously been seen on TiO₂ surfaces with NO₃⁻ ion bound onto Ti⁴⁺ sites and NO⁺ ion on O²⁻ sites.⁵⁰ Alternatively, as inferred from the peak shifts due to the electron delocalization in O 1s region, surface oxygen atoms can be involved into reaction directly to form adsorbed nitrate via (3)

By analogy with other metal oxides, NO₂ adsorption enthalpy, depending on its binding configuration, is relatively large (120–130 kJ/mol)^{51, 52} thus favoring product, Pb(NO₃)₂, formation.

The N1s spectrum of PbO reacted with 18 Torr H₂O (85% RH) shown in Figure 3 shows nitrate peak at 407.1 eV, slightly shifted towards lower binding energies and an additional peak at 403.6 eV. This lower binding energy peak is only apparent at the highest relative

humidity used (85 % RH) and can be assigned to several nitrogen containing species, with most likely due to that of surface nitrite, NO_2^- , as determined from XPS analysis of NaNO_2 particles.²³

Stable NO_2^- formation is possible via adsorption on Pb surface sites via O or N atoms with neighboring oxygen sites strongly hydroxylated and unavailable for further reaction

or via hydroxyl bound complex disproportionation reaction (6) by analogy with the mechanisms previously observed on $\gamma\text{-Al}_2\text{O}_3$ ⁵³

Similarly, the well-known surface-catalyzed hydrolysis of NO_2 can result in the formation of both nitric and nitrous acid with nitrous acid partitioning to the gas phase.^{54, 55}

Although surface nitrite species might be forming at lower relative humidity below 85 %RH, it is below the detection limit or there are gas-phase products forming like HONO. It should be noted that the quantification of N1s:Pb4f for this particular system is not straightforward. It can be seen in Figure 3 that as-received PbO and, as well as 38% RH (and higher) H_2O reacted samples have one set of doublets in the Pb4f region with Pb4f_{7/2} at 137.5 and 139.7 eV due to the Pb-O⁴⁶ and Pb-NO₃ bonds, respectively, whereas experiments done at 9 and 25% RH experiments have two distinct doublet pairs since at these lower RH values both surface species are present simultaneously.

The C1s binding energy region for all the particles show the main peak at 285.0 eV due to adventitious carbon, commonly used as a charge calibration reference.⁵⁶ Notably, while this peak was present in all the samples, another peak at 289.0 eV was only present in the unreacted PbO implying that the underlying carbon species is consumed or displaced by reaction. This peak is due to the adsorbed carbonate species, PbCO_3 ,⁵⁷ in support of the previous discussion on the complex nature of lead oxide surfaces in the environment. C1s:Pb4f ratio showed about 20% of surface sites covered by adventitious carbon or carbonate in the unreacted PbO sample.

The Pb4f region shows a doublet characteristic of Pb4f_{7/2} and Pb4f_{5/2} transitions. Pb4f peaks of unreacted PbO were located at 137.5 and 142.3 eV, consistent with previous literature values.⁴⁶ Elemental quantification was performed in terms of atomic ratios and it was found that PbO surface, e.g. ~3 nm distance where electrons can escape without inelastic scattering and O1s:Pb4f ratio was found close to unity, i.e. within the expected stoichiometry. Upon reaction with NO_2 , both peaks shifted to higher binding energies by ~1 eV. This shift was also observed on O1s region and can be attributed to the increase electronegativity of the layer formed upon reaction with NO_2 . Concurrently, a new peak appeared in Pb4f spectrum with Pb4f_{7/2} at 139.7 eV. This peak agrees very well with that of $\text{Pb}(\text{NO}_3)_2$, also shown in Figure 3. When PbO was further exposed to NO_2 at different relative humidity, all of the peaks in the Pb4f spectrum were shifted and assigned to

Pb(NO₃)₂ rather than PbO indicating that all of the surface depth investigated (estimated to be on the order of 3 nm) was converted into Pb(NO₃)₂. Additionally, the valence band (VB) region (0 to 28 eV) shows changes with a new feature at 14 eV due to adsorbed nitrate following PbO exposure to NO₂ as shown in Supporting Information Figure S1.

From the XPS data discussed above, it can be seen that relative humidity can change the amount of the adsorbed NO₂ product, possibly by exposing new surface layers for reactions and facilitate higher amount of NO₂ adsorption followed by consecutive dissolution. To further analyze relative humidity effects, PbO sample was *consecutively* exposed to NO₂ in the presence of increasing relative humidity. XPS spectra obtained following these different exposures were used to obtain adsorbed nitrogen product amount on the sample surface in terms of the N1s:Pb4f ratio shown in Figure 4. In this plot, experiments are shown for six consecutive NO₂ exposures and then analysis in the absence (circles) and presence of increasing relative humidity (squares). The N1s:Pb4f ratio shows that there is little change in the amount of adsorbed nitrogen product following NO₂ exposure in the absence of relative humidity. However, in the presence of relative humidity, it is seen that the adsorbed nitrogen product first increases as indicated by the N1s:Pb4f ratio but then at very highest relative the amount of adsorbed nitrogen goes down. These data are consistent with previous observations of Tompkins *et al.*⁵⁸ via gravimetric measurements showing high growth rate of Pb(NO₃)₂ thin film on tin-lead alloy upon the exposure to NO₂ at intermediate relative humidities (20–40%) with a very slow growth rate at very high relative humidities. Although it was postulated in that study that at high relative humidity with the presence of multilayers of water, the water layer was not uniformly spread out across the sample surface and this water clustering would result in decreased NO₂ reaction with lead surface sites. In our experiments, however, adsorbed nitrogen amount decreased with relative humidity after 25% RH showing removal of nitrogen-containing species with increase relative humidity.

Effect of NO₂ exposure on the dissolution of PbO particles

Dissolution experiments were performed of as-received PbO as well as on those reacted with NO₂ under various environmental conditions to investigate how mobility of PbO changes upon aging in the environment due to adsorption and reaction of trace atmospheric gases. Dissolution measurements compared PbO particles exposed to NO₂ or NO₂ and 8 Torr H₂O in an overnight evacuated reaction chamber for 24 hours to PbO samples that were not exposed to NO₂. NO₂-exposed samples were then suspended in distilled water (pH ~7) and dissolution experiments were performed with unreacted PbO being used as a reference. Dissolution data obtained from these experiments are shown in Figure 5. It can be seen that NO₂-exposed particles, for both NO₂ and NO₂+ 8 Torr water RH, had considerably more dissolved lead, between two and three fold, respectively, when compared to PbO particles that had not been exposed. To get a better understanding on the cause of this increase and relevant species involved, solubility product values for several relevant lead compounds are tabulated and given in Table 2 together with their corresponding literature sources.^{35, 59} It can be seen that none of the lead oxide, hydroxide or carbonate compounds are very soluble in water, while Pb(NO₃)₂ is highly soluble (59.7 g/100 g H₂O at 25°C). Lead nitrate formed on surface of PbO, thus, can be mobilized in aqueous solutions. Assuming the (100) plane with 7.7 site/nm² site density of orthorhombic PbO is available for reaction, about three PbO surface layers would react to obtain 120 ppm of lead in solution corresponding to ~6 Å Pb(NO₃)₂ layer formed. Although, powder XRD for NO₂-exposed PbO particles did not show any new peaks, these dissolution data and the XPS measurements suggest that thin film coatings, a few layers thick, of lead nitrate are formed. This agrees well with the observed low BET surface area of 0.4±0.2 m²/g. Notably, presence of relative humidity at 8 Torr (~38 % RH at room temperature) also enhanced the dissolved lead amount beyond the extent of that reacted with NO₂ only. This could be due to the enhanced NO₂ reactivity

towards PbO in the presence of relative humidity resulting in the greater uptake of adsorbed nitrogen species except at the highest relative humidity. This type of RH enhanced gas uptake has previously been observed for SO₂ adsorption on calcite surfaces and has been associated with the important role of adsorbed water in the reactivity of environmental interfaces under ambient conditions that include enhanced surface ion mobility due to adsorbed water that leads to exposed surface sites for further reaction.²⁴ Although no bulk lead nitrate formation was observed by XRD analysis, XPS and dissolution data suggest that although the reaction was surface limited it was a thin film coating containing several layers with a two fold increase in lead dissolution found following exposure to NO₂.

Environmental and health implications

The results of this study show that nitrogen dioxide can react with lead containing particles by forming adsorbed lead nitrates, which in turn can readily dissolve in solution and thus increase the mobilization of otherwise stationary sources of lead. The amount of dissolved lead increases nearly three-fold following exposure to NO₂. Although recent work by Edwards and co-workers showed increased lead mobility after exposure to NO₂ and O₃ mixture while concluding that a reaction with polymer binder was major factor in Pb release,¹⁸ it can be argued that another component of this observation is the formation of soluble lead salts that form in the case of NO₂ exposure due to the heterogeneous reaction chemistry of NO₂ with lead oxide surfaces. Once in solution phase, lead can remain soluble.⁶⁰ Other recent studies have shown that PbO powder, exposed to formaldehyde can yield Pb(HCO₂)₂ and secondary lead carbonate phases.⁶¹ Yadav and Sharma showed that both 4.5% lead nitrate or lead acetate in diet of mice severely damaged heme synthesis.⁶² Furthermore, lead nitrate films formed could easily react with organic compounds available in environment as carboxylic and humic acids in water⁶³ or isoprenes and other higher hydrocarbons⁶⁴ yielding organonitrates, as an alternative to other OH radical initiated mechanisms.⁶⁵ Organonitrates due to their volatility and lipid solubility are much more readily absorbed than inorganic lead compounds and can have enhanced toxicity, with confirmed organolead poisoning of the nervous system.⁴

Although the study discussed here were done at higher concentrations than those found in the atmosphere, these results show that heterogeneous chemistry of atmospheric gases with lead-containing particles and surfaces can play a role in the mobility of lead in the environment. Typical NO_x lifetime in the troposphere is in the order of several hours⁶⁶ due to the homogeneous reactions with O₃ and hydroxyl radicals, sufficient for the heterogeneous adsorption on atmospheric aerosols to proceed. Thus in order to fully understand the mobilization and toxicity of lead containing particle surfaces further studies on the adsorption and heterogeneous reactivity of trace atmospheric gases are further warranted.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

This material is based on work supported in part by the Environmental Health Sciences Research Center (EHSRC) pilot grant program funded by NIEHS NIH P30 ES05605. This material is also based on work partially supported by the National Science foundation under Grant CHE-0952605. Any opinions, findings, and conclusions or recommendations expressed in this material are those of the authors and do not reflect the views of the National Science Foundation. We thank Daniel Allman for help with XRD measurements.

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Figure 1.

SEM image and XRD powder diffraction of PbO particles. For comparison, XRD patterns of lead containing compounds and minerals, such as PbO (massicot), Pb metal, PbO (litharge), PbO_2 (plattnerite), Pb_3O_4 (minium), PbCO_3 (cerussite) and $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$ (hydrocerussite) are also shown.

Figure 2.

Survey XPS data of as-received PbO and after exposure with NO_2 . Inset: N1s binding energy region after exposure to NO_2 shows a new peak due to adsorbed nitrate species. See text for further details.

Figure 3.

High resolution XPS data in the O1s, N1s, C1s and Pb4f binding energy regions of as-received PbO and after exposure to NO₂ under various environmental conditions as noted in the left panel. For comparison, XPS data are also shown for a Pb(NO₃)₂ sample. The sloping background in the N1s region is from the intense Pb4d peak as seen in the survey spectra shown in Figure 2.

Figure 4.

Quantification of the nitrogen product following adsorption on PbO after six consecutive exposures to NO₂ for 30 min in the absence of water vapor (circles). Similarly, data following exposure to NO₂ at various relative humidity is shown (squares).

Figure 5. ICP-OES measured $\text{Pb}^{2+}(\text{aq})$ in solution from unreacted PbO particles and NO_2 exposed particles for 24 h, with NO_2 alone as well as NO_2 and 8 Torr H_2O mixture. Reactors contained solids loading of 50 g L^{-1} . Uncertainties represent one standard deviation from triplicate experiments.

Table 1

XPS binding energy assignments

Region	Assigned species	Binding Energy, eV	
		Current work ^a	Reference
O1s			
	O ²⁻ in Pb-O	528.9(529.6)	528.5 ⁴⁶
	OH ⁻ ; CO ₃ ²⁻	531.1(531.8)	531.2 ^{47, 48}
	NO ₃ ⁻	533.2	Pb(NO ₃) ₂ standard
N1s			
	NO ₃ ⁻	407.4	Pb(NO ₃) ₂ standard
C1s	C-C	285.0	285.0 ⁵⁶
	CO ₃ ²⁻	289.0	289.1 ⁵⁷
Pb4f			
	Pb ²⁺ in Pb-O	137.5 (138.5)	137.3 ⁴⁶
	Pb(NO ₃) ₂	139.7	Pb(NO ₃) ₂ standard

^aCalibrated to the C1s peak at 285.0 eV

Table 2Tabulated solubility products of lead compounds^a

Compound (mineral)	K _{sp}	Reference
PbO (litharge)	1.2×10^{-15}	Graedel et al. ⁵⁹
PbO ₂ (plattnerite)	3.2×10^{-66}	Graedel et al. ⁵⁹
Pb(OH) ₂	1.43×10^{-20}	CRC Handbook of Chemistry and Physics ³⁵
PbCO ₃ (cerussite)	7.4×10^{-14}	CRC Handbook of Chemistry and Physics ³⁵
Pb(NO ₃) ₂	Soluble 59.7 g/100 g H ₂ O at 25°C	CRC Handbook of Chemistry and Physics ³⁵

^aNo solubility data for PbO (mineral massicot) was found