Photo- and thermo-chemical transformation of AgCl and Ag$_2$S in environmental matrices and its implication$^*$

Yongguang Yin$^{a,b}$, Wei Xu$^c$, Zhiqiang Tan$^a$, Yanbin Li$^d$, Weidong Wang$^a$, Xiaoru Guo$^a$, Sujuan Yu$^a$, Jingfu Liu$^a,^*$, Guibin Jianga$^a$

$^a$ State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China
$^b$ Institute of Environment and Health, Jianghan University, Wuhan 430056, China
$^c$ Institute of High Energy Physics, Chinese Academy of Sciences, Beijing 100049, China
$^d$ Key Laboratory of Marine Chemistry Theory and Technology, Ministry of Education, Ocean University of China, Qingdao 266100, China

**Abstract**

AgCl and Ag$_2$S prevalently exist in the environment as minerals and/or the chlorination and sulfidation products of ionic silver and elemental silver nanoparticles (AgNPs). In this work, we investigated the chemical transformation of AgCl and Ag$_2$S under simulated sunlight (in water) and incineration (in sludge and simulated municipal solid waste, SMSW). In the presence of natural organic matter, AgCl in river water was observed to be transformed into AgNPs under simulated sunlight, while photo-reduction of Ag$_2$S could not take place under the same experimental conditions. During the course of incineration, pure Ag$_2$S was transformed into elemental silver while AgCl remained stable; however, both Ag$_2$S in sludge and AgCl in SMSW can be transformed to elemental silver under incineration, evident by the results of X-ray absorption spectroscopy and scanning electron microscopy measurements. Incineration temperature played an important role in the transformation of Ag$_2$S and AgCl into elemental silver. These results suggest that chemical transformations of Ag$_2$S and AgCl into elemental silver could be a possible source of naturally occurring or unintentionally produced AgNPs, affecting the fate, transport, bioavailability and toxicity of silver. Therefore, it is necessary to include the contributions of this transformation process when assessing the risk of ionic silver/AgNPs and the utilization and management of incineration residues.

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1. Introduction

The wide use of silver in the photographic industry, electronics and electrical equipment, silverware, coins, water purification, and other medical applications, makes the release of silver into the environment probable. By using material flow analysis techniques, it was estimated that the global silver discards account for approximately 57% of the silver mined (Johnson et al., 2005). More importantly, the amount of silver entering into landfills is comparable to that found in tailings (Johnson et al., 2005). Owning to their low solubility and high chemical stability (Levard et al., 2012), AgCl and Ag$_2$S are the most widely occurring silver species in the environment. AgCl and Ag$_2$S minerals, commonly known as chlorargyrite and acanthite, are the main forms of silver minerals in the nature (Migdisov et al., 1999; Stefansson and Seward, 2003). Ag$_2$S and AgCl can be formed in the corrosion layer of silver wares in the presence of moderate to high humidity (Graedel, 1992). Once encountered with Cl$^-$ or S$_2^-$, ionic silver can be quickly transformed into AgCl or Ag$_2$S due to favorable chemical thermodynamics (Levard et al., 2012). Nano- or micron-sized AgCl and Ag$_2$S particles have been observed in the wash water from conventional silver (ionic silver, AgCl, and metallic Ag) containing textiles, which came from the chlorination and sulfidation of dissolved silver ion or metallic silver (Mitrano et al., 2014). Similarly, once released into the environment, silver nanoparticles (AgNPs) can also undergo chlorination and sulfidation (Mitrano et al., 2014), greatly affecting the bioavailability and toxicity of silver (Levard et al., 2012). For example, after exposure to hypochlorite/detergent solution, over 50% AgNPs in the antimicrobial sock material were converted to AgCl (Impellitteri et al., 2009). Besides chlorination, sulfidation of
AgNPs is also a common transformation process of AgNPs in the environment, especially in raw wastewater and wastewater treatment plant (WWTP). Nano-sized Ag$_2$S was observed to be present in the final stage sewage sludge of a full-scale municipal wastewater treatment plant (Kim et al., 2010), which possibly derived from the in situ sulfidation of soluble Ag species or AgNPs under anaerobic conditions.

Most previous studies focus on the chlorination and sulfidation processes of ionic silver and AgNPs. However, little is known about the post-transformations of AgCl and Ag$_2$S in the environment. In consideration of the prevalent existence of AgCl and Ag$_2$S, understanding the post-transformations of AgCl and Ag$_2$S in the natural environment is important to further elucidate the fate and toxicity of ionic silver and AgNPs. In the presence of S$^2^-$, AgCl particles can be converted into more stable Ag$_2$S in the sewage sludge (Kaegi et al., 2015; Lombi et al., 2013). In addition, since AgCl can be converted into AgNPs in photography (Belloni, 2003), it is reasonable to hypothesize that this reduction process may also occur in natural water under sunlight. In contrast to AgCl, Ag$_2$S is more stable in the environment; however, transformations of Ag$_2$S have also been observed under certain environmental conditions (Thalmann et al., 2015; Li et al., 2016). It was recently found that ozone treatment can transform nano-sized Ag$_2$S in wastewater effluent into AgCl particles (Thalmann et al., 2015), while Ag$_2$S spiked into the sludge can be partially converted into elemental silver in bench-scale fluidized bed reactor and muffe oven under various incineration treatments at ~800 °C (Impellitteri et al., 2013; Meier et al., 2016). The mechanisms and controlling factors (e.g., temperature) for the transformations of AgCl and Ag$_2$S have yet to be elucidated. This knowledge is required for understanding the fate of ionic silver and AgNPs in the environment.

The objectives of this study were to investigate the chemical transformations of AgCl and Ag$_2$S (i) in natural water with natural organic matter (NOM) under sunlight, and (ii) in sludge and municipal solid waste (MSW) during the course of incineration under different temperature. To fulfill these aims, comprehensive characterization methods were used to probe the transformation of silver species, including UV-visible spectrometry (UV–vis), transmission electron microscopy (TEM), scanning electron microscopy (SEM), X-ray diffraction (XRD), and X-ray absorption spectroscopy (XAS). This work would be helpful for understanding the fate of ionic silver and AgNPs in the environment and managing wastes containing Ag$_2$S and AgCl.

2. Materials and methods

2.1. Materials

AgNO$_3$, AgCl, Ag$_2$S, Ag$_2$SO$_4$ and silver foil were purchased from Beijing Chemicals (Beijing, China). NaCl and Na$_2$S were from J&K Chemicals (Beijing, China). The other chemicals were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). Suwanee River natural organic matter (SRNOM, Lot No. 1R101N) was obtained from the International Humic Substance Society (St. Paul, MN). The dissolved organic carbon of the NOM solution was measured with a Phoenix8000 UV-persulfate total organic carbon analyzer (Tekmar-Dohrmann, Cincinnati, OH). All the reagents were used as obtained without further purification. Ultrapure water (18.3 MΩ) produced with a Milli-Q Gradient system (Millipore, Billerica, MA) was used throughout the study.

2.2. Photochemical transformation of AgCl and Ag$_2$S under simulated sunlight

AgCl and Ag$_2$S were prepared by adding 1.0 mmol L$^{-1}$ AgNO$_3$ and 1.2 mmol L$^{-1}$ NaCl or 0.6 mmol L$^{-1}$ Na$_2$S to 100 mL river water or NOM solution (Table S1). According to our previous studies (Yin et al., 2015, 2012, 2014b), the pH of surface water in Beijing is about 8.0. Thus, NOM solution with a pH of 8.0 (buffered by borate) was adopted in this study. Water from Chaobai River in Beijing was collected and filtered through a 0.22 μm glass fiber filter. The pH, inorganic ions, and dissolved organic carbon were measured (Table S2) ahead of the photochemical experiment. Due to the low solubility of AgCl and Ag$_2$S and limited amount of strong binding moieties in NOM (e.g. thiol group) (Rao et al., 2014), the main silver species should be AgCl or Ag$_2$S in the presence of Cl$^-$ or S$^{2-}$. By using the stability constant of Ag$^+$ with Cl$^-$ (Levart et al., 2012), the Ag species in river water and NOM solution were calculated, which showed that AgCl accounts for 71% and 66% of total Ag in river water and NOM solution, respectively. Similarly, in the presence of 0.6 mmol L$^{-1}$ S$^{2-}$, Ag$_2$S accounts for over 99% of total Ag in river water and NOM solution. The experiments were performed in 100 mL quartz glass bottles with quartz caps. The bottles were then placed in a solar simulator (TEM880, Befang Lihui, Beijing, China) equipped with three wind-refrigerated 2500 W Xe lamps. The spectrum of the simulated sunlight was measured in a previous study (Yin et al., 2014a). The intensity of the light was set as 550 W m$^{-2}$. During the course of experiment, the reaction temperature was maintained at ~35 °C using a water bath. Three mL aliquots were sampled at specific time intervals for UV–vis and TEM characterization.

2.3. Transformation of AgCl and Ag$_2$S under incineration

For pure AgCl and Ag$_2$S, the AgCl or Ag$_2$S powder (1000 mg) was added into a ceramic crucible and then incinerated in a muffe furnace (Vulcan 3–1750, York, PA) at various temperatures (200–900 °C) for 4 h, respectively. Sludge was sampled from Qinghe WWTP (Beijing, China). Upon arrival at the laboratory, the sludge was freeze-dried, ground and sieved. Total organic carbon (TOC) was analyzed by an O.I. solids TOC analyzer (O.I. Analytical, USA). Briefly, about 50 mg of sample was placed into the pre-combusted quartz sample cup. Before the analysis, phosphoric acid (1.0 mol L$^{-1}$) was added to remove the inorganic carbon. TOC concentration in the sludge was measured to be 721 mg g$^{-1}$. SMSW was prepared according to the MSW composition reported in literature, including food waste (45%), building waste (30%), wood (5%), plastics (8%), glass (1%), paper (7%), and textile (4%) (Feng et al., 2010). These materials were mixed and milled with a grinder. In consideration of the low sensitivity of XAS, a relatively higher concentration of Ag$_2$S or AgCl (at 5000 mg Ag kg$^{-1}$ level) was spiked into the sludge and SMSW, respectively. A sewage sludge survey by the United States Environmental Protection Agency showed that the Ag concentrations in sewage sludge range from 1.94 to 856 mg kg$^{-1}$ (dry sludge) (USEPA, 2009). Concentrations of Ag up to 1860 mg kg$^{-1}$ (wet sludge) were observed in the sludge fed with silver-containing industrial wastewater (Maeng and Pavlovlathis, 1996). Considering the non-uniform spatial distribution of temperature in furnaces and various thermal treatment processes for sludge/MSW treatment (Weticher and Ogada, 1999; Zorpas et al., 2001), transformations of Ag$_2$S/AgCl in sludge/SMSW at a variety of temperatures, from 300 to 900 °C (4 h), were investigated.

The differential thermal analysis (DTA)–thermogravimetric analysis (TGA) for characterization of the thermal stability of Ag$_2$S and AgCl were carried out on the Derivatograph (MOM, Budapest, Hungary) apparatus under the following conditions: air or N$_2$ atmosphere, heating rate 10 °C min$^{-1}$ up to 1000 °C, and using alumina as the reference material.
2.4. Characterization of the species of silver

UV–vis spectra were recorded using a UV–vis-Near Infrared Spectrophotometer (UV–3600, Shimadzu, Japan). The wavelength scanning was performed from 200 to 1000 nm at a 0.5 nm wavelength interval.

To distinguish and quantify AgNPs in the AgCl solution, a method based on AgCl selective dissolution-ultrafiltration-inducively coupled plasma mass spectrometry (ICP-MS) was developed. Briefly, 0.1% (w/v) Triton X-114 was added into the AgNPs/AgCl suspension, serving as coating agent to prevent the dissolution of AgNPs. Then, 10 mmol L$^{-1}$ Na$_2$S$_2$O$_3$ was added to dissolve AgCl particles. After shaking for 15 min, the solution was added into the Amicon Ultra-15 centrifugal filter (with 3 kDa nominal molecular weight cut-off) (Millipore, Darmstadt, Germany). After centrifugation at 8422 g for 40 min, the filtrate was diluted by 5% HNO$_3$ for Ag$^+$ determination by ICP-MS. The concentration of AgNPs was calculated by subtracting Ag$^+$ concentration from the total silver concentration. The recovery test demonstrated that most AgCl (>97.9%) was dissolved by adding Na$_2$S$_2$O$_3$, while the dissolution of AgNPs was negligible (<0.5%).

TEM and energy dispersive spectrometry (EDS) analyses were carried out with a high resolution TEM coupled with an EDS at 200 kV (TECNAI G20, FEI, Hillsboro, OR). TEM samples were prepared by dropping 5 μL aliquots of the aqueous sample onto an ultrathin carbon-coated copper grid and drying at room temperature.

XRD patterns were recorded with an X'pert PRO instrument (PANalytical, Almelo, Netherlands) using Cu Kα radiation ($λ$ = 0.15418 nm), with the diffraction angle (2θ) at a range of 30–90°. For the aqueous sample, the solution containing nanoparticles was centrifuged at 14, 000 g and then the collected precipitate was analyzed using XRD characterization after drying on a glass slide.

X-ray photoelectron spectroscopy (XPS) analysis was carried out in an Escalab 250 spectrometer (Thermo Scientific, UK) using monochromatized Al Kα radiation of energy 1486.6 eV. The incineration residue samples were mounted on a stainless steel holder and core level binding energies were determined using C1s peak at 284.8 eV as the charge reference. An incident monochromated X-ray beam from the Al target (15 kV, 10 mA) was focused on a 500 μm spot size to the sample surface. The base pressure of the ultrahigh vacuum chamber was 2 × 10$^{-9}$ mbar.

The SEM was performed using a field emission SEM (SU-8020, Hitachi, Japan) coupled with EDS (INCA X, Oxford) with 3000 V accelerating voltage and 8600 nA emission current. In the EDS measurement, the beam voltage and takeoff angle were set as 15.0 kV and 35.0°, respectively.

The Ag K-edge X-ray absorption fine structure spectroscopy (XAFS) was performed at beamline BL14W1, Shanghai Synchrotron Radiation Facility. The Ag standards analyzed included Ag foil, Ag$_2$O, Ag$_2$S, AgCl, Ag$_2$SO$_4$, AgNO$_3$, and Ag-cystine. The Ag standards and ash samples were finely ground and pressed into pellets for XAFS analysis. Given that the K-edge of silver is 25514 eV, the Si (311) double crystal monochromator was employed to scan the incident X-ray energy. The X-ray absorption spectra of samples and reference standards were collected in transmission mode using ionic chambers filled with air. The XAFS data were collected over ~200 eV to 900 eV from the K-absorption edge. All spectra of samples and standards are normalized after subtracting the background using AUTOBK algorithm in IFEFFIT package (Ravel and Newville, 2005). The near-edge parts of the XAFS spectra are good indicators for speciation and reflect the local atomic coordinate environment. The linear combination fitting (LCF) method implemented in Athena software was applied to analyze the near-edge part of XAFS, e.g. –20 eV–100 eV from the absorption Ag K-edge. The goodness of fitting was evaluated by R-factor, defined as follows:

$$R = \frac{\Sigma (exp - fit)^2}{\Sigma exp^2}$$

3. Results

3.1. Photochemical transformation of AgCl and Ag$_2$S under simulated sunlight

Photochemical transformation of AgCl and Ag$_2$S in river water was investigated to reflect the fate of in situ generated AgCl and Ag$_2$S. After spiking AgNO$_3$ into the river water, the solution turned into pale white, indicating the formation of AgCl due to the presence of Cl$^-$ in river water (80.5 mg L$^{-1}$, as shown in Table S1). After spiking AgNO$_3$ into the mixture of river water and NaCl or Na$_2$S, the solution turned quickly into white or black, respectively, suggesting the formation of AgCl and Ag$_2$S. When NaCl, AgNO$_3$ and Na$_2$S were sequentially added into the river water, the solution color became white first and then turned black, indicating the replacement of Cl$^-$ by S$^{2-}$ owning to its lower K$_{sp}$ (K$_{sp}$ (AgCl) = 1.77 × 10$^{-10}$; K$_{sp}$ (Ag$_2$S) = 1.6 × 10$^{-49}$) (Levard et al., 2012). Precipitations of AgCl and Ag$_2$S were not observed within the experimental time, indicating that the two species of Ag are stable in natural water due to the stabilization effect of NOM (Yin et al., 2015). These results suggested that once released into the aquatic environment, silver ion from direct discharge or dissolution of AgNPs can react with Cl$^-$ and S$^{2-}$ ubiquitously presented in natural water to form AgCl or Ag$_2$S.

The XRD patterns demonstrated that under simulated sunlight irradiation, AgCl but not Ag$_2$S could be partially transformed into elemental silver in the river water (Fig. 1). In contrast, under dark conditions, only signals from AgCl or Ag$_2$S were observed, demonstrating the important role of irradiation in the formation of elemental silver. As for Ag$_2$S, the spiking of S$^{2-}$ into the river water completely inhibited the generation of elemental AgNPs, regardless of the presence of Cl$^-$ or not. The UV–vis spectra (Fig. S1) for the river water spiked with or without Cl$^-$ showed a broadened absorbance at about 600 nm, which was assigned to the larger or

![Fig. 1. XRD patterns of Chaobai River water spiked with AgNO$_3$ under different experimental conditions. Detailed experimental information was given in Table S1.](image-url)
aggregated AgNPs (Chinnapongse et al., 2011). Further light irradiation resulted in “redshift” and disappearance of the surface plasmon resonance peak from AgNPs, which is ascribed to the reduction-induced fusion and sedimentation of AgNPs (Yin et al., 2012, 2014a). In contrast, in the presence of S2−, the surface plasmon resonance peak at about 500 nm is observed, which is suspected to be from Ag2S aggregates (Fang et al., 2013). Unlike Cl−, no significant change of UV–vis spectra was observed in the presence of S2− under simulated sunlight irradiation, suggesting Ag2S may be more stable and resistant to photo-reduction. The results of TEM and EDS analyses were consistent with those from XRD and UV–vis. Elemental AgNPs were detected after exposure to simulated sunlight irradiation, with or without NaCl spiking (Figs. S2 and S3). The distance between lattice planes observed in TEM images (Fig. S2b and Fig. S3b) indicated that these nanoparticles were face-centered cubic (fcc) silver metals. In the presence of S2−, only chain-like structured Ag2S was observed (Figs. S4 and S5). Results of this study on the basis of a variety of techniques suggest that AgCl is photo-sensitive and can be photo-chemically transformed to elemental AgNPs in river water, whereas Ag2S is very stable under sunlight.

To further validate the reductive role of NOM, the photochemical transformation of AgCl and Ag2S in NOM solution was further investigated. The XRD (Fig. S6), UV–Vis (Fig. S7), TEM and EDS (Figs. S8–S13) results confirmed the findings in river water, i.e., AgCl but not Ag2S can be transformed into AgNPs under simulated sunlight irradiation. Quantitative analysis of AgNPs in the AgCl solution by selective dissolution-ultrafiltration-ICP-MS further revealed that, after exposure to simulated light irradiation for 4 h, the spiking of Cl− into the NOM solution (Sample 2 in Table S1) significantly enhanced the formation of AgNPs (from 27.8 ± 1.0% to 59.4 ± 3.6%). This finding suggests that in comparison with Ag+, AgCl may be more favorable to be transformed to AgNPs under light irradiation (Kracht et al., 2015).

3.2. Transformation of AgCl and Ag2S under incineration

DTA and TG were performed for analyzing thermal stability of Ag2S and AgCl. As shown in Fig. S14, the DTA curve for Ag2S under air showed an endothermic peak at −181 °C, corresponding to the transformation of monoclinic crystal Ag2S to body centered crystal Ag2S (Glazov and Burkhanov, 1980). The endothermic peak at −547 °C corresponded to the further transformation of body centered crystal Ag2S to face centered crystal Ag2S (Glazov and Burkhanov, 1980). The TG curve showed a mass loss which started from −500 °C and became faster from −800 °C. The largest mass loss (14.2%) was achieved at −830 °C, which corresponds to the stoichiometric loss of sulfur in Ag2S (12.9%). This result also indicated that the transformation of Ag2S to elemental Ag could occur during thermal treatment. In contrast, negligible mass loss was observed for Ag2S under N2, indicating O2 may be essential for the formation of elemental silver via promoting the oxidation of S2−. The DTA curve for AgCl under air showed an endothermic peak at −450 °C, corresponding to the melting of AgCl powder (Lou et al., 2011). The mass loss was observed from 700 to 1000 °C which may be caused by the partial volatilization of AgCl (Visnapuu and Jensen, 1970). To simulate the incineration process, pure Ag2S or AgCl powder was put in the muffle furnace and heated at incineration temperature from 200 to 900 °C for 4 h. The incineration residues were characterized by XRD to probe the possible chemical transformation (Fig. 2). For Ag2S (Fig. 2a), no significant chemical transformation was observed at temperatures lower than 500 °C, consistent with the results of TG. It should be noted that although phase transformation of γ–Ag2S to β– and γ–Ag2S was found in the DTA, no significant peaks of β– and γ–Ag2S were observed by the XRD. This was possibly ascribed to the transformation of β– and γ–Ag2S back into α–Ag2S again in the cooling procedure (Blanton et al., 2011). From 500 to 600 °C, the XRD showed a transformation of Ag2S to Ag2SO4. In addition, when the temperature was higher than 500 °C, the peaks at 38.3°, 44.2°, 64.7°, 77.4°, and 81.6°, corresponding to the (111), (200), (220), (311) and (222) lattice plane of metallic silver, increased and the peaks of Ag2S decreased, confirming the transformation of Ag2S to face centered crystal structured metallic silver. Correspondingly, the color of incineration residues turned from black into gray and further into silvery white. For AgCl (Fig. 2b), no significant change was observed at temperatures less than 500 °C. However, the incineration residues were transformed from white particles into transparent gel at temperatures higher than 500 °C, suggesting the melting of AgCl at higher temperature. This was consistent with the DTA results of AgCl. At all incineration temperatures, no XRD peak for elemental silver was observed in the AgCl incineration.

Considering the possible occurrence of Ag2S in sludge from WWTP and AgCl in MSW, the transformation of Ag2S and AgCl under incineration was further investigated in the matrices of sludge and SMSW, respectively. The incineration residues were characterized by X-ray photoelectron spectroscopy (XPS) and XAS. The Cl 1s signal of XPS (Fig. S15) for sludge showed that the loss of carbon occurred at temperatures between 300 and 400 °C. The O1s signal (Fig. S16) suggested that, with the increasing incineration temperature, the fraction of phenolic/alcoholic oxygen (at −533.5 eV) decreased and the oxygen fraction from metallic oxide (at −531 eV) increased. From the S2p signal (Fig. S17) we can clearly see that the sulfide (at −163 eV) signal disappeared at 900 °C, suggesting the oxidation of sulfide.

By using LCF of XAFS at the silver K-edge using the reference standards, the speciation of silver in the incineration residues can be evaluated (He et al., 2013). As shown in Fig. 3a–c, the XAFS spectra of silver reference (sulfur foil (elemental silver), Ag2S, Ag2SO4, AgCl, AgNO3), incineration residue of sludge and SMSW spiked with Ag2S and AgCl were well distinguished. The XAFS fingerprints of incineration samples (Fig. 3b and c) evidently showed that the XAFS spectra of silver changed after incineration at high temperature, indicating the possible transformation of silver species. Detailed analysis of the XAFS spectra by LCF (i.e., the percentage contribution of each silver species for incineration sample at various temperatures) was summarized in Table 1. The low R factor values indicated that the LCF analysis fitted most of the tested samples well. The relatively higher R factor for some of the ash samples (Ag2S-500 °C and AgCl-900 °C) suggested that other silver species may also be present in the ashes. As shown in Table 1, without incineration (at room temperature) or with incineration at low temperature (300 °C), Ag2S in sludge was stable and its transformation was negligible. This result also indicated that the potential beam reduction of silver during XAS data collection is negligible. After incinerating at 500 °C for 4 h, 51% of Ag2S was transformed into elemental silver, while the rest (49%) was transformed into Ag2SO4. With further increase of incineration temperature, the fraction of elemental silver decreased to 20%, while the fraction of Ag2SO4 increased to 80%. The temperature-dependent transformation of silver species was different from the above XRD results for incineration of pure Ag2S, which may be due to the effects of organic matter in the sludge. For the SMSW with the addition of AgCl, at 300 °C incineration, 22% AgCl was transformed into elemental silver, while 78% of AgCl remained unchanged. When the incineration temperature increased to 700 °C, the fraction of AgCl increased to 92% and elemental silver decreased correspondingly to 8%. At 900 °C, the fraction of elemental silver further decreased to 4%, and 62% of AgCl was transformed into ionic silver species, e.g., AgNO3. We also tried to fit the XAS data for the
ash (AgCl-900 °C) by Ag2SO4. However, the R factor of the results was too high to be acceptable (data not given). These results indicate that in the ash (e.g., AgCl-900 °C), Ag(I) is weakly coordinated with other atoms (e.g., oxygen atom) like AgNO3 (Meyer et al., 1976), in contrast to a stronger coordination in Ag2SO4 (Penner and Li, 2004). Our previous study showed that pure AgCl could not be transformed into elemental silver under incineration, inconsistent with the findings in the SMSW. This may be due to the existence of organic matter in the matrix which can serve as an electron donor in the incineration procedure. These above results demonstrated that under incineration, Ag2S in sludge and AgCl in MSW can partially be transformed into elemental silver.

The incineration residues of sludge from the WWTP were further characterized by SEM and EDS. As shown in Fig. 4, a number of white spots were observed, ranging from hundreds nm to 1 µm (Fig. 4a). Corresponding EDS (Fig. 4b) suggested that elemental silver was the major species in this marked spot, together with small amounts of S (the molar ratio of Ag/S = 50.8) (Fig. 4a). The EDS mapping of Ag and S (Fig. 4c and d) validated this opinion. All these results demonstrated that after incineration, Ag2S in sludge may be transformed into elemental silver particles. Similar results were observed for the incineration residue of SMSW spiked with AgCl, in which elemental silver particles were evident (Figs. S18a and b), although the EDS in Fig. S18b also showed that there is still unreacted AgCl (the molar ratio of Ag/Cl = 3.9). In addition, as shown in Figs S18c and d, a qualitative correlation between Ag and Cl was observed in the EDS mapping, indicating there is residual AgCl even after incineration.

4. Discussion

The speciation of silver in fresh water is controlled by chelating ligands (especially thiol, S2− and Cl−), redox potential, and pH. Owing to thermodynamic constraints, Ag2S and AgCl are deemed to be the major silver species, into which ionic silver and AgNPs will be transformed under environmental conditions (Reactions (1)–(4)) (Levard et al., 2012). AgCl, Ag2S, as well as Ag0 were theoretically calculated to be possible species of Ag in fresh water.
Levard et al., 2012). AgCl and Ag₂S in environmental waters can originate from both the direct discharge (e.g. laundry discharge) (Kaegi et al., 2015) and the transformation (chlorination (Levard et al., 2013b) and sulfidation (Levard et al., 2011)) of ionic silver and AgNPs because of their low solubility products and high thermodynamic stability (Levard et al., 2012).

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4Ag^0 + O_2 + 4H^+ \rightarrow 4Ag^+ + 2H_2O \quad (1)
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\[
Ag^+ + Cl^- \rightarrow AgCl \quad (2)
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Table 1
Linear combination fitting results of XAFS for the Ag₂S spiked sludge and AgCl spiked SMSW before and after incineration at various temperatures.

| Sample                                    | Ag₂S (%) | AgCl (%) | Elemental Ag (%) | Ag₂SO₄ (%) | AgNO₃ (%) | R factor \times 1000 |
|-------------------------------------------|----------|----------|------------------|------------|-----------|---------------------|
| Ag₂S-RT                                   | 100      | -        | -                | -          | -         | -                   |
| (Ag₂S spiked sludge at room temperature)  |          |          |                  |            |           |                     |
| Ag₂S-300 °C                               | 100      | -        | -                | -          | -         | -                   |
| (Ag₂S spiked sludge, incinerated at 300 °C)|          |          |                  |            |           |                     |
| Ag₂S-500 °C                               | -        | -        | 51               | 49         | -         | 0.546               |
| (Ag₂S spiked sludge, incinerated at 500 °C)|          |          |                  |            |           |                     |
| Ag₂S-700 °C                               | -        | -        | 31               | 69         | -         | 0.065               |
| (Ag₂S spiked sludge, incinerated at 700 °C)|          |          |                  |            |           |                     |
| Ag₂S-900 °C                               | -        | -        | 20               | 80         | -         | 0.149               |
| (Ag₂S spiked sludge, incinerated at 900 °C)|          |          |                  |            |           |                     |
| AgCl-RT                                   | -        | 100      | -                | -          | -         | -                   |
| (AgCl spiked SMSW at room temperature)    |          |          |                  |            |           |                     |
| AgCl-300 °C                               | -        | 78       | 22               | -          | 0         | 0.017               |
| (AgCl spiked SMSW, incinerated at 300 °C) |          |          |                  |            |           |                     |
| AgCl-500 °C                               | -        | 94       | 7                | -          | 0         | 0.101               |
| (AgCl spiked SMSW, incinerated at 500 °C) |          |          |                  |            |           |                     |
| AgCl-700 °C                               | -        | 92       | 8                | -          | 0         | 0.119               |
| (AgCl spiked SMSW, incinerated at 700 °C) |          |          |                  |            |           |                     |
| AgCl-900 °C                               | -        | 35       | 4                | -          | 62        | 0.600               |
| (AgCl spiked SMSW, incinerated at 900 °C) |          |          |                  |            |           |                     |

Fig. 4. SEM (a), EDS (b), and X-ray fluorescence scan of S (c) and Ag (d) for Ag₂S spiked sludge after incineration at 500 °C.
Although the occurrence of AgCl and Ag₂S has been theoretically predicted and identified in the environment, the post-transformation of AgCl and Ag₂S have yet been well understood. In photography, AgCl can be transformed into Ag⁰ in the presence of both photosensitizer and irradiation (Kolter, 2009). Recently, photocatalytic conversion of AgCl into AgNPs mediated by DNA (Wang et al., 2011, 2015) and peptides (Kracht et al., 2015) was observed. These previous studies suggest that photo-reduction of AgCl in the fresh water should also be highly possible in the presence of an environment-related photo-sensitizer (e.g. NOM), as demonstrated in this work. In the absence of NOM, photo-reduction of AgCl could not occur, proving that AgCl itself cannot serve as the electron donor (Kracht et al., 2015). The detected photo-reduction of Ag⁺ and AgCl to AgNPs in NOM solution suggested that, besides as a capping agent to disperse the formed AgNPs (Yin et al., 2014a), NOM may also serve as a photo-sensitizer for providing electron to reduce free Ag⁺ and AgCl (Reaction (5and 6)).

\[
\text{AgCl} + \text{NOM}_\text{red} \xrightarrow{hv} \text{Ag}^0 + \text{NOM}_\text{ox} \quad (5)
\]

\[
\text{AgCl} + \text{NOM}_\text{red} \xrightarrow{hv} \text{Ag}^0 + \text{Cl}^- + \text{NOM}_\text{ox} \quad (6)
\]

Compared with free Ag⁺, the presence of AgCl microcystals can facilitate the recombination of the reduced Ag⁰ atom to form silver clusters and nanoparticles at the surface of AgCl-NOM particles (Kracht et al., 2015). Our study showed that the photo-conversion of Ag⁺ into AgNPs was enhanced by the co-occurrence of Cl⁻, demonstrating the critical role of AgCl in photo-reduction of Ag⁺ in environmental waters. Our results also demonstrated that in the presence of S²⁻, both Ag⁺ and AgCl can be transformed into Ag₂S. Recently, Kaegi et al. also reported that during the 800 m transport in the sewer channel (travel time of ~30 min), AgCl in liquid discharge could be transformed into nanoparticulate Ag₂S (Kaegi et al., 2015). As Ag₂S is resistant to photo-reduction, it is more persistent in aquatic system compared to Ag⁺ and AgCl. However, a recent study by Thalmann et al. discovered that ozonation of WWTP effluent can oxidize S²⁻ in nano-Ag₂S and subsequently transform nano-Ag₂S into AgCl particles (Thalmann et al., 2015). Our results, combined with Thalmann’s, indicate that Ag₂S could be potentially transformed into elemental AgNPs by ozonation and subsequent photo-reduction.

Various silver species (including elemental silver, AgNPs, ionic silver and AgCl) are commonly incorporated into textiles to prohibit the growth of bacteria (Mitrano et al., 2014). Elemental silver, ionic silver, and AgNPs, can be readily transformed into AgCl in the washing procedure (Impellitteri et al., 2009; Mitrano et al., 2014). In industrial laundry, an AgCl suspension may be also applied to soak the textiles at the end of the washing process for protection purposes (Kaegi et al., 2015). The resulting AgCl associated with the disposal of textile products can be introduced into the MSW with high concentration. The discharged silver (as ionic silver, AgCl, and AgNPs), from daily life and industry, can also enter the water system, further be transformed into Ag₂S and enriched in the sludge at high concentration (Kaegi et al., 2015; Kim et al., 2010; Maeng and Pavlostathis, 1996; USEPA, 2009). A previous study has demonstrated that Ag₂S in sludge or biosolids remained stable throughout 50 years of weathering and aging under ambient environmental conditions (Donner et al., 2015). However, in recent years, sludge/MSW incineration is becoming one of the most widely used waste-treatment methods, which is characterized by volume reduction, stabilization, pathogen elimination, and recycling (Wu et al., 2014). It was reported that incineration treatment accounts for 22% of sludge final disposal in the US (USEPA, 1999) and 19% of that in EU countries (Kelessidis and Stasinakis, 2012), respectively. Our simulated incineration study revealed that “inert” Ag₂S can be transformed into elemental silver particle in nano- or micro-size in the presence of sludge (Reaction (7)). Although no elemental silver particle was observed in the incineration of pure AgCl powder, AgCl can also be partly transformed into elemental silver particles in the presence of SMSW, indicating the critical role of organic matter in SMSW in the thermal transformation of AgCl. In addition, ionic silver species (e.g. Ag₂SO₄), which are more toxic than “inert” AgCl and Ag₂S, were also identified in the incineration residue (Reaction (8)) (Choi et al., 2008; Leward et al., 2013a; Xi et al., 2012).

\[
\text{Ag}_2\text{S} + \text{O}_2 \xrightarrow{d} 2\text{Ag} + \text{SO}_2 \uparrow \quad (7)
\]

\[
\text{Ag}_2\text{S} + 2\text{O}_2 \xrightarrow{d} 2\text{Ag}_2\text{SO}_4 \quad (8)
\]

These photochemical and incineration processes not only are possible sources of naturally occurring or unintentionally produced AgNPs, but also have potential impacts on the fate of ionic silver and engineered AgNPs (Pourzahedi and Eckelman, 2015). More importantly, considering the different toxicity of various silver species (Choi et al., 2008; Reinsch et al., 2012), the conversion of AgCl and Ag₂S to AgNPs and ionic silver could potentially increase the toxicity of silver. Therefore, the chemical transformation processes of AgCl and Ag₂S should be taken into account when assessing their toxicological impacts in natural water or solid wastes, especially during the utilization and management of silver-containing incineration residue.

5. Conclusions

In this study, the chemical transformation of AgCl and Ag₂S was investigated under simulated sunlight (in water) and incineration (in sludge and SMSW) by using comprehensive characterization techniques. The obtained results suggested that, in the presence of NOM, AgCl in river water can be transformed into AgNPs under simulated sunlight, while photo-reduction of Ag₂S was not observed under the same conditions. Both Ag₂S in sludge and AgCl in SMSW can be transformed to elemental silver under incineration, evident by the results of X-ray absorption spectroscopy and scanning electron microscopy measurements. However, considering the relative higher concentration of silver used in our study, further research at environmental concentration leveled silver is still need to elucidate its transformation in a real environment. Nevertheless, our results suggest that chemical transformations of Ag₂S and AgCl into elemental silver could be a possible source of naturally occurring or unintentionally produced AgNPs, potentially affecting the fate, transport, bioavailability and toxicity of silver.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.envpol.2016.10.081.

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