

The interaction between atrazine and the mineral horizon of soil: a spectroscopic study

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Abstract

Purpose In this paper, an attempt was made to explain the long-lasting occurrence of atrazine in soil. Despite the fact that this herbicide has been banned in European Union 10 years ago, it is still detected in the environment.

Materials and methods Soil samples (organic and mineral horizon), SiO₂ and Al₂O₃ sorbents were spiked with atrazine. The ultrasound-assisted extraction coupled with gas chromatography-electron capture detector was performed to establish the atrazine recovery depending on the type of soil horizon and sorbent. Fourier transform infrared spectroscopy (FTIR) analysis was conducted to determine the type of interactions between atrazine and sorbents.

Results and discussion The atrazine recovery was lower for the mineral horizon (15%) compared to the organic horizon (63%). This finding suggests an interaction between atrazine and the mineral components of soil. Therefore, attempts have been made to explain atrazine's interaction with the main mineral components of soil, SiO₂ and Al₂O₃, and to investigate the influence of pH on atrazine's behaviour in soil. The atrazine recoveries were 86.5 and 10.7% for Al₂O₃ and SiO₂, respectively. The obtained results demonstrated that the

protonated atrazine exhibits stronger interactions with the soil mineral layer (recovery below 0.1%) in comparison to molecular form of atrazine (recovery 86%). FTIR results suggested interactions between atrazine and SiO₂. FTIR analysis revealed that 1,3,5-azidine ring interacts with SiO₂ molecule.

Conclusions In acidic soil, atrazine remediation is limited, especially if the soil contains minerals with high SiO₂ contents. This situation may cause the long-lasting persistence of atrazine in soil.

Keywords Atrazine · FTIR · Interaction · Mineral horizon · Soil

1 Introduction

The triazine group of herbicides is the most well known and has been widely used around the world for more than 50 years. Triazines accumulate in leaves and meristems, where they inhibit the Hill reaction by blocking photosynthesis by binding with tyrosinase, the enzyme responsible for the oxidation of polyphenols to quinones (Mou et al. 2011). The simplicity and low cost of atrazine (2-chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine) synthesis make it the most popular triazinic compound herbicide. It is a selective herbicide that is applied at a rate of 1 kg ha⁻¹ to corn, sorghum, sugarcane, pineapple fields and orchards as well as applied to non-agricultural lands to control broad-leaf and grassy weeds. Although it has been banned in European Union countries, it is still in use in other regions of the world. For instance, in the USA, almost 30,000 t of atrazine are applied annually (Hase et al. 2008). Because of its intense use, stability and ability to translocate in the environment (Roustan et al. 2014; Yixin et al. 2014; Nachimuthu et al. 2016), atrazine is present in soils and waters worldwide (Hase et al. 2008; Merini et al.

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2009; Feria-Reyes et al. 2011; Li et al. 2012; Farlin et al. 2013; Geng et al. 2013; Ji et al. 2015; Ouyang et al. 2016a). Atrazine is suspected to be an endocrine disruptor and is linked to Parkinson's disease in humans (Filipov et al. 2007; Brodeur et al. 2009). Atrazine has also been reported to exhibit reproductive toxicity in mammals (Wilhelms et al. 2006; Weselak et al. 2007).

The fate of atrazine after it enters the soil is dependent on its sorption properties, water solubility, polarity and its ionic nature. The physico-chemical characteristic of atrazine is presented in Table 1. Other factors that influence atrazine's stability in soil are its texture, organic matter content, water content, the presence of microorganisms and the soil pH (Wang et al. 1999).

Minerals and organic matter (humic substances, HS) in soil, which are differentiated into fulvic acids, humic acids and humin, are largely responsible for the adsorption of atrazine (Ouyang et al. 2016b). The binding of atrazine to HS has been the subject of many research papers (Neto et al. 1994; Garbin et al. 2007; Prosen et al. 2007; Dutta et al. 2011), but the complex interactions are the reason for a controversy discussion on the mechanisms by which these substances are bound: electron transfer, hydrogen bonding, proton transfer resulting in ionic bonds or partitioning into the hydrophobic domains of HS. Other researchers explain the formation of well-known non-extractable chloro-s-triazine residues in soil by chemical binding to HA by heteroatomic bonds after the substitution of a chlorine atom (Neto et al. 1994; Yu and Cole 1997; Davies and Jabeen 2003; Prosen and Zupancic-Kralj, 2005, Prosen et al. 2007). Many researchers have demonstrated the influence of the mineral components of soil on the sorption of atrazine (Davies and Jabeen 2003; Gonzalez-Pradas et al. 2003; Lesueur et al. 2008; Feria-Reyes et al. 2011; Barchanska et al. 2013; Prado et al. 2014). SiO₂ and Al₂O₃ are the predominant minerals present in soil. The mineralogical composition of soil includes quartz, plagioclase, kalifeldspar, calcite, mica, kaolinite and residual phase (clay minerals) (Norra et al. 2008). The role of minerals on atrazine adsorption in soil is not well documented. Gilchrist et al. (1993) found that the adsorption capacity of clays for atrazine followed the order of montmorillonite > illite > kaolinite.

The literature review and the results of our experiments (Barchanska et al. 2013) prompted us to carry out a more comprehensive study on the interaction between atrazine and selected mineral compounds in soil.

The present work aims to contribute to a better understanding of atrazine's interactions with the main inorganic constituents of clay minerals, silica and alumina and to investigate the influence of pH on atrazine's behaviour in soil.

As a tool for atrazine determination in soil samples, ultrasound-assisted extraction (UAE) coupled with gas chromatography-electron capture detector (GC-ECD) was chosen. This extraction technique does not provide recovery

Table 1 Physico-chemical characteristic of atrazine (PPDB)

Parameter	Value
Solubility in water (mg L ⁻¹ , 22 °C, pH 7)	33
logK _{ow} (25 °C)	2.5
Soil sorption constant, K _{oc}	100
Melting point (°C)	171–174
Vapour pressure (20 °C; × 10 ⁶ mmHg)	0.3
Henry's law constant (Pa m ⁻³ mol ⁻¹)	1.5 × 10 ^{-4*}
pK _a	1.70

percentages as high as microwave-assisted extraction (MAE), but it does not break the bond between atrazine and inorganic soil components (Gevao et al. 2000); therefore, it is suitable for the investigation of the interaction in the herbicide-soil matrix. For the investigation of atrazine's interaction with the selected mineral compounds, Fourier transform infrared spectroscopy (FTIR) and elemental analysis were applied.

2 Materials and methods

2.1 Chemicals and reagents

The standard for atrazine was obtained from Riedel-de Haën (Seelze, Germany). Atrazine stock standard solution was prepared by dissolving atrazine in methanol.

Methylene chloride, sodium hydroxide and hydrochloric acid, which were all of analytical grade, were provided by CHEMPUR (Piekary Sl. Poland). The characteristics of Al₂O₃ (Bellefonte, PA, USA) and SiO₂ used (Merck, Darmstadt, Germany) are shown in Table 2.

2.2 Instrumentation

Qualitative and quantitative chromatographic analyses were performed using a PerkinElmer Clarus 500 gas chromatograph (GC) (Waltham, MA, USA) equipped with an electron capture detector (ECD) and a 30 m × 0.25 mm i.d. DB-5MS column with a film thickness of 0.25 μm.

The column temperature was programmed to increase from 150 to 275 °C at a rate of 10 °C min⁻¹, maintain for 3 min and then increase from 275 to 300 °C at a rate of 16 °C min⁻¹. The temperature of the injector was 250 °C, and the temperature of the detector was 310 °C.

The investigated compound was identified by its retention time. The qualitative analysis was performed using the external standard method. Limit of detection was calculated as three times the signal to noise ratio, whereas the limit of quantification, determined as three times the limit of detection, was equal to 4.5 ng g⁻¹.

Table 2 Physical characteristic of sorbents

Parameter	Al ₂ O ₃	SiO ₂
Particle size	150	70–230
Surface area (mm ² g ⁻¹)	155	450–540
Pore size (Å)	56	60
pH	9.5	7.5

For atrazine extraction from the soil samples, an ultrasound bath POLSONIC 2 (Warsaw, Poland) with a frequency of 40 kHz and ultrasound power of 2×100 W was used.

The infrared spectra of atrazine and the mixtures of atrazine and sorbents 1 as reported in Figs. 1 and 2 were recorded at room temperature (25 °C) in the frequency range 4000–400 cm⁻¹ with a Fourier transform infrared spectrophotometer 40FTS BioRad (Hercules, CA, USA) using 32 scans and a resolution of 2 cm⁻¹. Samples were analysed as KBr pellets.

The soil composition was determined using a wavelength-dispersive X-ray fluorescence spectrometer manufactured by RIGAKU ZSX Primus (Japan).

2.3 Sample preparation

2.3.1 Soil sample preparation

This study consisted of preparing atrazine-spiked soil samples from pesticide-free soil collected in a forest from the surface layer (organic horizon) and from a depth of 1 m (mineral horizon). The detailed characteristics of primary soil samples are shown in Table 3.

Soil pH was determined according to ISO 10390:2005, the Kappena method was used for hydrolytic acidity determination and the sum of exchangeable cations was found according to the Pallman procedure. On the basis of these data, the sorption capacity was calculated. The organic carbon content was determined according to ISO 14235:1998. Stones and fragments of plants were removed from the soil samples. Next, the soil was homogenised and dried on blotting paper until air-dried. Finally, it was ground and sieved through a 0.8-mm sieve. Since the objective of this study was the interaction between atrazine and mineral horizon of soil, the following procedure was applied to remove low-molecular hydrophobic compounds as well as any possible residues of the pesticide. One hundred grams of sieved soil was weighed into a 250-mL conical flask, and 125 mL methylene chloride was added; UAE was conducted for 20 min. This procedure was repeated three times. Subsequently, the solvent was decanted and the soil was air-dried. One millilitre of atrazine standard solution in methanol (0.15 mg mL⁻¹) was added to 1 g of the prepared soil, and the sample was left in the dark at room temperature for 24 h. After adsorption of atrazine, the extraction step was

performed to establish the atrazine recovery depending on the type of soil (organic or mineral horizon).

2.3.2 Sorbent preparation

To 1 g of dried (at 180 °C for 24 h) SiO₂, the following substances were added:

- A. 0.5 mL of water
- B. 0.5 mL of 0.1 M NaOH
- C. 0.5 mL of 6 M HCl

Subsequently, the samples were homogenised and left in the dark at room temperature for 24 h. Next, 1 mL of atrazine solution in methanol (0.15 mg mL⁻¹) was added, and the sample was left in the dark at room temperature for 24 h. Each type of sample was prepared six times.

Al₂O₃ was calcinated at 405 °C for 24 h. Next, 1 mL of atrazine solution in methanol (0.15 mg mL⁻¹) was added to 1 g of sorbent, and the sample was left in the dark at room temperature for 24 h.

2.4 Extraction

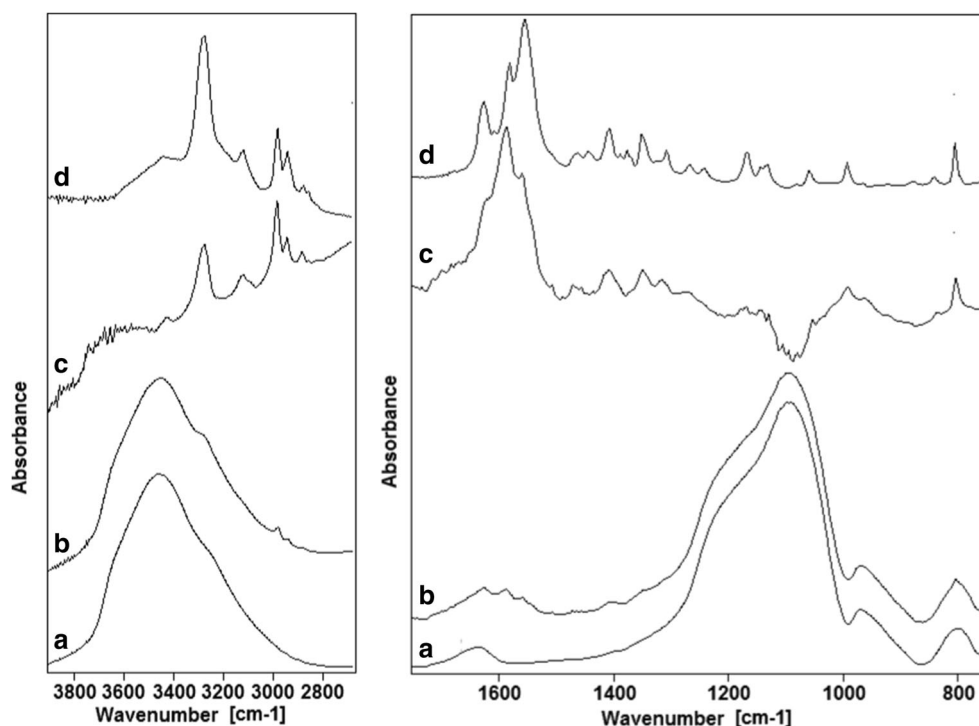
The ultrasound-assisted extraction was conducted for both the soil and sorbent samples (5.0 g). Methylene chloride was applied as a solvent (55 mL). The total extraction time was 60 min (in three 20-min stages each with fresh solvent). The extraction was conducted at room temperature. Next, the samples were filtrated, and the extracts were concentrated on a rotary evaporator to a volume of 1 mL. Finally, the extract was completely dried to a dryness solid at room temperature. Before the chromatographic analysis, it was dissolved in 1 mL of hexane (Barchanska et al. 2013).

3 Results and discussion

The literature overview indicates that the atrazine recovery from soil samples is strongly influenced by the extraction technique, the pH of the soil and the herbicide's interaction with the organic and inorganic compounds in the soil matrix (Gonzalez-Pradas et al. 2003; Urena-Amate et al. 2005; Barchanska et al. 2013). The sorption and desorption processes of atrazine on soil components play an important role in its environmental behaviour. Efforts have been made to study the various physical and chemical mechanisms of atrazine sorption onto humic substances (Sposito et al. 1996) and clay minerals (Herwig et al. 2001), respectively.

Taking into account the diverse physico-chemical properties of heterogeneous soil, especially the coexistence of two different main components, i.e., organic matter (humic and fulvic acids) and mineral phase (mainly aluminosilicates),

Fig. 1 FTIR spectra of SiO₂ (a), SiO₂ spiked with atrazine after extraction procedure (b), the spectrum obtained after subtracting spectrum a from spectrum b (c) and spectrum of atrazine (d)



the effectiveness of atrazine extraction from soil is influenced by non-specific interactions between this herbicide and the soil matrix. To explain these interactions, three parallel series of soil samples were collected in forest areas from the upper layer (organic horizon), which contains humus, as well as from a depth of 1 m, where the concentration of humus is considerably lower than in the organic horizon.

Low recovery of atrazine from soil samples obtained using ultrasound-assisted extraction was reported in earlier studies

(Baranowska et al. 2006; Barchanska et al. 2013). The effectiveness of extraction was not influenced by the type of solvent. Therefore, this assessment of the influence of soil pH and moisture content on atrazine sorption was undertaken. The organic horizon and mineral horizon exhibit different physical–chemical profiles, which are presented in Table 3. The organic carbon content, hydrolytic acidity and sorption capacity are higher for the organic horizon than for the mineral horizon, but the pH values of both horizons are similar. The

Fig. 2 FTIR spectra of Al₂O₃ (a), Al₂O₃ spiked with atrazine after extraction procedure (b), the spectrum obtained after subtracting spectrum a from spectrum b (c) and spectrum of atrazine (d)

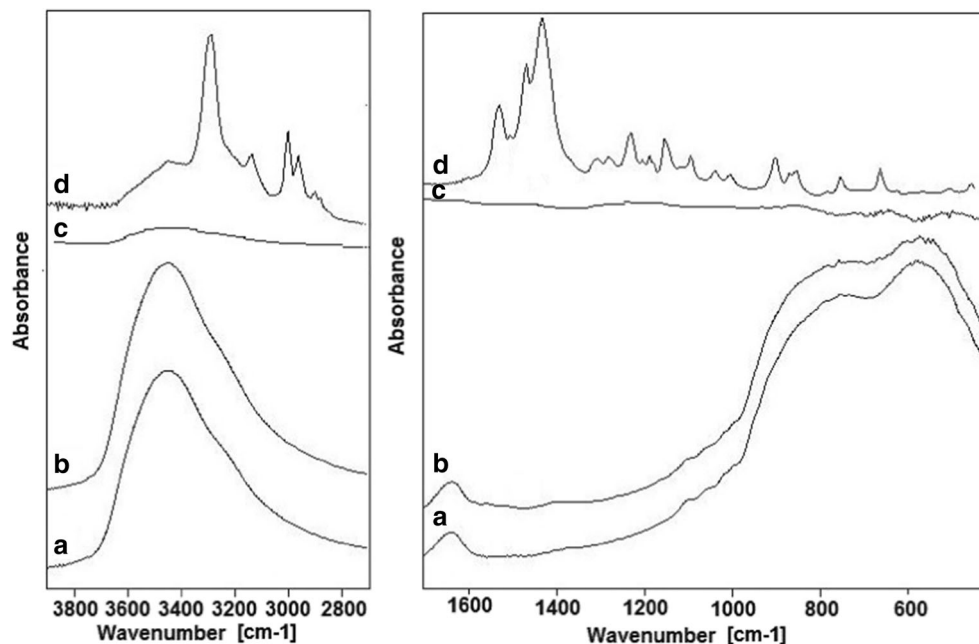


Table 3 Characteristic of investigated soil and atrazine recovery

Parameter	Organic horizon	Mineral horizon
pH in H ₂ O	6.20	6.30
Hydrolytic acidity, Hh (cmol(+) kg ⁻¹)	2.21	0.53
Sorption capacity (%)	8.50	3.49
Organic carbon content (%)	18.45	0.60
Sum of exchangeable cations (%)	6.29	1.23
Soil mineral composition (%)		
MgO	0.25	0.37
Al ₂ O ₃	1.45	6.37
SiO ₂	21.72	88.30
K ₂ O	0.66	1.56
CaO	0.79	0.47
Fe ₂ O ₃	0.59	1.30
C _{total}	25.5	0.9
Atrazine recovery, % (standard deviation, SD, %)	63 (4)	15 (3)

n = 3

XRF analysis revealed that the mineral horizon contained 88% SiO₂ and 6.4% Al₂O₃, while the organic horizon contained 21.7% SiO₂ and 1.45% Al₂O₃ (Table 3). The recovery rates of atrazine from the organic horizon, which is rich in organic compounds, and the mineral horizon (1 m depth) are given in Table 3.

The obtained results show that the atrazine recovery rate (Table 3) was 63.1% for the organic horizon, whereas its recovery from the mineral horizon, where SiO₂ dominates, was 15.4% (Table 3). In our previous research (Barchanska et al. 2013), the low recovery rate (15%) of atrazine from soil samples was obtained using UAE rather than MAE, which had a recovery rate of approximately 84%. Low atrazine recovery rates yielded by UAE were also noted by Lesueur et al. (2008) and Baranowska et al. (2006). The adsorption isotherms of this process indicate that desorption efficiency is low (Deng et al. 2010).

The differences in atrazine recovery from the organic and mineral horizons are most likely caused by the different compositions (ratio of organic matter to mineral compounds) of these soil layers. The obtained results indicate that the atrazine extraction efficiency was definitely lower for the mineral horizon, which exhibits a lower sorption capacity and sum of exchangeable cations than the organic horizon. This finding suggests an interaction between atrazine and the mineral components of soil, particularly SiO₂ (Davies and Jabeen 2003). Deng et al. (2010) reported that the average percentage of atrazine that was desorbed from sandy loam soil was 32.3 ± 6.0%. These data suggested that atrazine would remain bound to the sandy loam soil. The interactions between organic and mineral compounds in soil are the result of van der Waals forces, cation bridges and ion exchange. The reason

for ion exchange and chemical sorption is the negatively charged, non-compensated electric charges that occur on the surface of soil colloids. The adsorption of humic and fulvic acids onto the loamy minerals occurs in the presence of multivalent cations.

The influence of minerals on atrazine's behaviour in soil is not well known. Gonzalez-Pradas et al. (2003) and Urena-Amate et al. (2005) investigated the adsorption of atrazine onto kerolite [Mg₃Si₄O₁₀(OH)₂·nH₂O]. The results demonstrated that atrazine is adsorbed onto the kerolite surface as a non-ionic species. The adsorption mechanism possibly occurs via cation bridging, which involves the formation of an inner-sphere complex between the kerolite Mg²⁺ cations and the atrazine -NH group. Cation bridges are formed by multivalent cations, which are able to create the bonds with charges occurring on the surface of the minerals and functional groups of humic compounds (i.e., COO⁻). Usually, such bridges are formed by the following cations: Ca²⁺, Fe³⁺ and Al³⁺. Considering the composition of the mineral horizon (1.3% Fe₂O₃ and 6.4% Al₂O₃), this type of interaction should not significantly influence the atrazine adsorption.

According to Davies and Jabeen (2003), atrazine is adsorbed onto bentonite, montmorillonite and humic acid by protonation and through hydrogen bonding. The hydrolysis of atrazine occurred on the surface of kaolinite. The clay minerals in soil play a major role in the metabolism of atrazine. Atrazine's hydrolysis to hydroxyatrazine and the formation of bound residues were mainly responsible for the observed hysteresis in its sorption and desorption isotherms.

SiO₂ is the main mineral component of soil; therefore, for the investigation of the non-specific interactions between atrazine and mineral compounds of soil, this sorbent was chosen

as a model. To estimate the influence of cation bridges formed by Al_2O_3 , the sorption experiments were also conducted using alumina.

In the case of Al_2O_3 , the mean recovery of atrazine was 86.5%, while for SiO_2 , it was only 10.8%. The detailed data are presented in Table 4.

The results of the elemental analysis of the SiO_2 -atrazine mixture, after herbicide extraction, revealed the presence of nitrogen in the SiO_2 sorbent, which may suggest the presence of triazine residue in the silica gel.

These differences in atrazine extraction efficacy between Al_2O_3 and SiO_2 resulted from the physical-chemical properties of atrazine (Table 1) and the properties of these sorbents (Table 2). To complete the description of the phenomena that occur in the mineral horizon of soil, the influences of water (pore solution) and pH were investigated in detail.

Atrazine was extracted from SiO_2 as described in Sects. 2.3.2 (A–C) and 2.4. The effectiveness of atrazine desorption from SiO_2 containing water (0.5 g g^{-1}) was 4.9% and was lower in comparison with dry sorbent (Table 4). When the pH of the sorbent was 1.0, atrazine recovery was lower than 0.1%. Similar results were obtained by Saint-Fort and Visser (1988) for the atrazine adsorption of clay minerals. The atrazine recovery rate was higher in alkaline conditions than in an acidic environment. The investigation of the pH dependence of the adsorption of atrazine onto silica gel was presented by Kovaios et al. (2010). They showed that the surface charge of the adsorbent is an important factor. A decrease of the solution pH from the equilibrium pH of 6.1 to 3.3 resulted in very little increase of the adsorbed atrazine. For higher pH values, the difference in atrazine adsorbed at the equilibrium pH was significant. The detailed results are presented in Table 4.

Aluminium occurs in soils in both the soil solution and the solid phase. Porous alumina provides a weak Lewis acidity and basicity as well as a low Bronsted acidity; the $\text{p}K_a$ of the Bronsted sites is 8.5 (Grun et al. 1996). Weathering of primary minerals initially proceeds through hydrolytic breaking of the Si–O–Al linkages in the primary minerals, thereby releasing Al^{3+} to the aqueous phase (Hiradate et al. 1998). The presence of alumina ions enhanced atrazine hydrolysis because they act as Lewis acids (Comber 1999; Ghauch et al. 1999).

Different types of hydroxyl groups exist on the silica gel surface: free, isolated –OH groups; active, bonded with the same or contiguous silica atom; bonded, with two, three or four other –OH groups within 2.52–2.6 Å; and geminate, –OH groups bonded with the same silica atom. The presence of SiO_2 in soil caused an increase in the hydrophilic character of the surface; therefore, the water sorption is higher. Amorphous silica has a weak Bronsted acidity due to the silanol groups. At higher temperatures under laboratory conditions, silica can develop Lewis acidity and basicity due to the activation of siloxane groups during the course of dehydration (Grun et al. 1996, Kromidas 2005).

Table 4 Atrazine recovery study

Sorbent	Atrazine recovery, % (standard deviation, SD, %)
Al_2O_3	86.3 (0.3)
SiO_2 (dry)	10.8 (0.2)
SiO_2 (pH 6.7)	4.9 (0.3)
SiO_2 (pH 1.0)	< 0.1
SiO_2 (pH 7.6)	6.2 (0.4)

$n = 3$

Because the pH of Al_2O_3 is 9.5, atrazine was in its molecular, non-hydrolysed form, in contrast to SiO_2 , which possesses acidic properties. Moreover, atrazine recovery from silicon dioxide may be influenced by the structure of this sorbent and a non-specific interaction between this herbicide and SiO_2 . As a result of interactions with the Bronsted acidic sites present on the silica gel surface, the retention of alkaline atrazine is higher than those obtained for alumina. The atrazine recovery rates from the studied sorbents are inversely proportional to their surface area.

Atrazine recovery from soil may also be influenced by the pore solution. Pore solutions contain dissolved sugars, fulvic acids and other organic acids, as well as inorganic compounds, such as nitrate, ammonium, potassium, phosphate, sulphate, calcium, zinc, iron and copper ions. These compounds are exchanged with the mineral and humic components of soil by adsorption. The soil pH can affect the type and number of ions that the soil solution contains. These ions can be exchanged between the soil and biological organisms. The organically bound Al in soil has been considered to be the major source of Al in solution, and its role in regulating Al^{3+} activity has been established (Matzner et al. 1998).

The recovery study suggests that the strength of the interaction forces between atrazine and the soil matrix compounds depends on the molecular form of the herbicide. In low pH conditions, atrazine exists in its protonated form, which is strongly bonded to the soil. In high pH conditions, atrazine is unprotonated; thus, it is weakly bonded to the soil matrix, which is in agreement with the findings presented by Browne (Browne et al. 1980). The influence of water content and the sorbent pH on the sorption of atrazine indicates the ionic character of the interaction between SiO_2 and the herbicide.

To explain the mechanism of the interaction between atrazine and SiO_2 , Fourier transform infrared spectroscopy was applied.

3.1 FTIR studies

In a series of IR studies, Davies and Jabeen (2003) found that atrazine is adsorbed onto bentonite and montmorillonite by protonation and/or the formation of hydrogen bonds. The

relatively small electrostatic effect measured may be attributed to the relatively low extent of atrazine protonation. Xing et al. (1996) also suggested that the azo and amino nitrogen atoms of atrazine can act as hydrogen bond acceptors with silanol groups or strongly adsorbed water molecules. In our studies of the nature of atrazine-silica gel interactions the FTIR method was used. The FTIR spectra obtained for SiO₂, atrazine and the residue obtained after atrazine extraction from SiO₂ are presented in Fig. 1.

The main features of the SiO₂ spectrum are the characteristic band at 1093 cm⁻¹ with a shoulder at 1200 cm⁻¹ (Fig. 1), which corresponds to the Si–O–Si stretching vibrations. The broad peak with maximum at 3442 cm⁻¹ corresponds to the stretching vibrations of hydroxyl groups and indicates the presence of water, which is additionally confirmed by a relatively weak peak at 1653 cm⁻¹ (deformation vibrations of OH groups). In the atrazine spectrum, the bands observed at 3472 and 3272 cm⁻¹ are characteristic of the amine groups, while these at 2974 and 2935 cm⁻¹ are originated from CH₃ and CH groups stretching vibrations. The bands attributed to the stretching vibrations of the 1,3,5-triazine ring appear at 1623, 1578 and 1552 cm⁻¹. The band observed at 1552 cm⁻¹ is partially overlapped by the band deriving from the deformation vibrations of the amine groups. In the region of 1450–1300 cm⁻¹ appear several bands due to deformation vibrations of this ring and two bands characteristic of the deformation vibrations of the CH₃ groups (1460 and 1348 cm⁻¹). At 804 cm⁻¹, middle intensity and relatively sharp band attributed to the stretching vibrations C–Cl groups are observed. The remaining, rather, weak bands correspond to the deformation vibrations of the 1,3,5-triazine ring, C–H groups (in triazine ring and in chains) and C–H₃ groups.

In the spectrum of the residue obtained after atrazine extraction from SiO₂, bands originating both from SiO₂ and atrazine can be found. After subtracting the SiO₂ spectrum from the spectrum of the extraction residue, the final spectrum is similar to that of atrazine; however, some features are different. It concerns the region due to atrazine vibrations, especially the stretching vibrations; the bands at 1623, 1578 and 1552 cm⁻¹ shift to 1621, 1587 and 1557 cm⁻¹, respectively. Moreover, the proportions between them are changed. These changes indicate that 1,3,5-azidine ring interact with SiO₂ molecule. In the spectrum obtained after subtraction of SiO₂ spectrum from the residue obtained after atrazine extraction from SiO₂, the bands attributed to the N–H group stretching vibrations (3472 and 3272 cm⁻¹) are quite the same as in the case of atrazine spectrum. It excludes the participation of the amine groups in interactions with SiO₂. Additionally, in the FTIR spectrum of the residue obtained after atrazine extraction from SiO₂, a difference in the shape of the Si–O–Si bands is observed. These changes confirm the presence of interactions between Si–O groups from silica gel and 1,3,5-triazidine ring from atrazine and exclude the hydrogen bond formation in that case.

In opposite to SiO₂, the spectrum of residue obtained after atrazine extraction from for Al₂O₃ is quite the same as that obtained for Al₂O₃ (Fig. 2). This confirms the lack of interactions between Al₂O₃ and atrazine.

4 Conclusions

1. The protonated atrazine exhibits stronger interactions with the soil mineral layer.
2. The results indicate that the soil pH influences atrazine behaviour in real soil samples. In acidic soil, atrazine remediation is limited, especially if the soil contains minerals with high SiO₂ contents. This situation may cause the long-lasting persistence of atrazine in soil.
3. FTIR analysis of spiked sorbent after extraction procedure revealed that 1,3,5-azidine ring interacts with SiO₂ molecule. The FTIR spectra do not unambiguously prove the existence of hydrogen bonds between atrazine and SiO₂.
4. FTIR studies showed the lack of interactions between Al₂O₃ and atrazine.

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References

- Baranowska I, Barchanska H, Pacak E (2006) Procedures of trophic chain samples preparation for determination of triazines by HPLC and metals by ICP-AES methods. *Environ Pollut* 143:206–211
- Barchanska H, Czaplicka M, Giemza A (2013) Simultaneous determination of selected insecticides and atrazine in soil by MAE-GC-ECD. *Arch Environ Prot* 39:27–40
- Brodeur JC, Svartz G, Perez-Coll CS, Marino DJG (2009) Comparative susceptibility to atrazine of three developmental stages of *Rhinella arenarum* and influence on metamorphosis: non-monotonous acceleration of the time to climax and delayed tail resorption. *Aqua Toxicol* 91:161–170
- Browne JE, Feldkamp JR, White JL, Hem SL (1980) Potential of organic cation-saturated montmorillonite as treatment for poisoning by weak bases. *J Pharma Sci* 69:1393–1395
- Comber SDW (1999) Abiotic persistence of atrazine and simazine in water. *Pest Sci* 55:696–702
- Davies JED, Jabeen N (2003) The adsorption of herbicides and pesticides on clay minerals and soils. Part 2. Atrazine. *J Incl Phenom Macro Chem* 46:57–64
- Deng J, Jiang X, Hu W, Hu L (2010) Quantifying hysteresis of atrazine desorption from a sandy loam soil. *J Environ Sci* 22:1923–1929
- Farlin J, Gallé T, Bayerle M, Pittois D, Braun C, El Khabbaz H, Lallement C, Leopold U, Vanderborght J, Weihermueller L (2013) Using the long-term memory effect of pesticide and metabolite soil residues to estimate field degradation half-life and test leaching predictions. *Geoderma* 207:15–24

- Feria-Reyes RP, Medina-Armena P, Teutli-Leon M, Garcia-Jimenez MG, Gonzalez I (2011) A new approach for atrazine desorption, extraction and detection from a clay-silty soil samples. *Am J Anal Chem* 2:63–68
- Filipov NM, Stewart MA, Carr RL, Sistrunk SC (2007) Dopaminergic toxicity of the herbicide atrazine in rat striatal slices. *Toxicology* 232:68–78
- Garbin JR, Milori DMBP, Simoes ML, da Silva WTL, Neto LM (2007) Influence of humic substances on the photolysis of aqueous pesticide residue. *Chemosphere* 66:1692–1698
- Geng Y, Ma J, Jia R, Xue L-q, C-j T, C-j L, Ma X, Lin Y (2013) Impact of long-term atrazine use on groundwater safety in Jilin Province. *China J Integr Agric* 12:305–313
- Gevaio B, Semple KT, Jones KC (2000) Bound pesticide residues in soils: a review. *Environ Pollut* 108:3–14
- Ghauch A, Rima J, Amine C, Martin-Bouyer M (1999) Rapid treatment of water contaminated with atrazine and parathion with zero-valent iron. *Chemosphere* 39:1309–1315
- Gilchrist GF, Gamble DS, Kodama H, Khan SU (1993) Atrazine interactions with clay minerals: kinetics and equilibrium of sorption. *J Agric Food Chem* 41:1748–1755
- Gonzalez-Pradas E, Socias-Viciano M, Saifi M, Urena-Amate MD, Flores-Cespedes F, Fernandez-Perez M, Villafranca-Sanchez M (2003) Adsorption of atrazine from aqueous solution on heat treated kerolites. *Chemosphere* 51:85–93
- Grun M, Kurganov AA, Schacht S, Schulz F, Unger KKK (1996) Comparison of an ordered mesoporous aluminosilicate, silica, alumina, titania and zirconia in normal-phase high-performance liquid chromatography. *J Chromatogr A* 740:1–9
- Hase Y, Tatsuno M, Nishi T, Kataoka K, Kabe Y, Yamaguchi Y (2008) Atrazine binds to F1F0-ATP synthase and inhibits mitochondrial function in sperm. *Biochem Biophys Res Comm* 366:66–72
- Herwig U, Klump E, Schwuger MJ, Narres HD (2001) Physicochemical interactions between atrazine and clay minerals. *App Clay Sci* 18: 211–222
- Hiradate S, Taniguchi S, Sakurai K (1998) Aluminum speciation in aluminum–silica solutions and potassium chloride extracts of acidic soils. *Soil Sci Soc Am J* 62:630–636
- Hutta R, Góra R, Halko R, Chalanyova M (2011) Some theoretical and practical aspects in the separation of humic substances by combined liquid chromatography methods. *J Chromatogr A* 1218:8946–8957
- ISO 10390:2005 (2005) Soil quality—determination of pH
- ISO 14235:1998 (1998) Soil quality—determination of organic carbon by sulfochromic oxidation
- Ji Y, Dong C, Kong D, Lu J (2015) New insights into atrazine degradation by cobalt catalyzed peroxymonosulfate oxidation: kinetics, reaction products and transformation mechanisms. *J Hazard Mater* 285:491–500
- Kovaios ID, Paraskeva CA, Koutsoukos PG (2010) Adsorption of atrazine in packed beds. *Global NEST J* 12:279–287
- Kromidas S (2005) More practical problem solving in HPLC. Weinheim, Wiley–VCH
- Lesueur C, Gartner M, Mentlem A, Fuerhacker M (2008) Comparison of four extraction methods for the analysis of 24 pesticides in soil samples with gas chromatography-mass spectrometry and liquid chromatography-ion trap-mass spectrometry. *Talanta* 75:284–293
- Li X, Wu T, Huang H, Zhang S (2012) Atrazine accumulation and toxic responses in maize *Zea mays*. *J Environ Sci* 24:203–208
- Matzner E, Pijpers M, Holland W, Manderscheid B (1998) Aluminum in soil solution of forest soils, influence of water flow and soil aluminum pools. *Soil Sci Soc Am J* 62:445–454
- Merini LJ, Bobillo C, Cuadrado V, Corach D, Giulietti AM (2009) Phytoremediation potential of the novel atrazine tolerant *Lolium multiflorum* and studies on the mechanisms involved. *Environ Pollut* 157:3059–3063
- Mou RX, Chen MX, Cao ZY, Zhu ZE (2011) Simultaneous determination of triazine herbicides in rice by high-performance liquid chromatography coupled with high resolution and high mass accuracy hybrid linear ion trap-orbitrap mass spectrometry. *Anal Chim Acta* 76:149–156
- Nachimuthu G, Halpin NV, Bell MJ (2016) Effect of sugarcane cropping systems on herbicide losses in surface runoff. *Sci Total Environ* 557–558:773–784
- Neto ML, Vieira EM, Sposito G (1994) Mechanism of atrazine sorption by humic acid: a spectroscopic study. *Environ Technol* 28:1867–1873
- Norra S, Fjer N, Fanwei L, Chu X, Xie X, Stube D (2008) The influence of different land uses on mineralogical and chemical composition and horizonation of urban soil profiles on Qingdao. *China J Soils Sed* 8:4–16
- Ouyang W, Huang W, Wei P, Hao F, Yu Y (2016a) Optimization of typical diffuse herbicide pollution control by soil amendment configurations under four levels of rainfall intensities. *J Environ Manag* 175:1–8
- Ouyang W, Zhao X, Tysklind M, Hao F (2016b) Typical agricultural diffuse herbicide sorption with agricultural waste derived biochars amended soil of high organic matter content. *Water Res* 9:156–163
- PPDB Pesticide Properties DataBase, accessed 12.06.2017
- Prado B, Duwig C, Hidalgo C, Müller K, Mora L, Raymundo E, Etchevers JD (2014) Transport, sorption and degradation of atrazine in two clay soils from Mexico: andosol and vertisol. *Geoderma* 232–234:628–639
- Prosen H, Zupancic-Kralj L (2005) Evaluation of photolysis and hydrolysis of atrazine and its first degradation products in the presence of humic acids. *Environ Pollut* 133:517–529
- Prosen H, Fingler S, Zupancic-Kralj L, Drevenkar V (2007) Partitioning of selected environmental pollutants into organic matter as determined by solid-phase microextraction. *Chemosphere* 66:580–1589
- Roustan A, Aye M, De Meo M, Di Giorgio C (2014) Genotoxicity of mixtures of glyphosate and atrazine and their environmental transformation products before and after photoactivation. *Chemosphere* 108:93–100
- Saint-Fort R, Visser SA (1988) Study of interactions between atrazine, diazinon and lindane with humic acids of various molecular weights. *J Environ Sci Heal A* 23:613–624
- Sposito G, Martin-Neto L, Yang A (1996) Atrazine complexation by soil humic acids. *J Environ Qual* 25:1203–1209
- Urena-Amate MD, Socias-Viciano M, Gonzalez-Pradas E, Saifi M (2005) Effects of ionic strength and temperature on adsorption of atrazine by a heat treated kerolite. *Chemosphere* 59:69–67
- Wang D, Shin JY, Cheney MA, Sposito G, Spiro TG (1999) Manganese dioxide as a catalyst for oxygen-independent atrazine dealkylation. *Environ Sci Technol* 33:3160–3165
- Weselak M, Arbuckle TE, Wigle DT, Krewski D (2007) In utero pesticide exposure and childhood morbidity. *Environ Res* 103:70–86
- Wilhelms KW, Cutler SA, Proudman JA, Carsia RV, Anderson LL, Scanes CG (2006) Lack of effects of atrazine on estrogen-responsive organs and circulation hormone concentrations in sexually immature female Japanese quail (*Coturnix coturnix japonica*). *Chemosphere* 65:674–681
- Xing B, Pignatello JJ, Gigliotti B (1996) Competitive sorption between atrazine and other organic compounds in soils and model sorbents. *Environ Sci Technol* 30:2432–2438
- Yixin Y, Hongbin C, Pai P, Hongmiao B (2014) Degradation and transformation of atrazine under catalyzed ozonation process with TiO₂ as catalyst. *J Haz Mat* 279:444–451
- Yu Y, Cole RB (1997) Micellar electrokinetic capillary chromatography method for direct determination of herbicides in Lake Pontchartrain, Louisiana, sediments. *Environ Sci Technol* 31:3251–3257