

# Contents

<b>Summary</b>	<b>ix</b>
<b>Zusammenfassung</b>	<b>xi</b>
<b>1 Introduction</b>	<b>1</b>
1.1 Arsenic – a global threat to human health .....	1
1.2 The fate of arsenic in the environment .....	2
1.3 Natural organic matter in the environment.....	6
1.4 Interactions between arsenic and natural organic matter .....	8
1.5 Research objectives and approach .....	11
1.6 References .....	14
<b>2 Bisulfide reaction with natural organic matter enhances arsenite sorption: Insights from X-ray absorption spectroscopy</b>	<b>23</b>
2.1 Introduction .....	24
2.2 Materials and methods.....	26
2.2.1 Materials.....	26
2.2.2 Organic sorbents .....	26
2.2.3 Peat characterization .....	27
2.2.4 Reaction of peat and HA with S(-II).....	27
2.2.5 Arsenite sorption.....	28
2.2.6 X-ray absorption spectroscopy .....	28
2.3 Results and discussion .....	30
2.3.1 Characterization of the organic sorbents .....	30
2.3.2 Reaction of peat and HA with S(-II).....	30
2.3.3 Sulfur K-edge X-ray absorption spectroscopy .....	32
2.3.4 Arsenite sorption.....	33
2.3.5 Arsenic K-edge X-ray absorption spectroscopy.....	34
2.3.6 Environmental implications .....	39
2.4 Supporting information .....	41
2.4.1 Evaluation of S K-edge XANES spectra of reference compounds.....	41
2.4.2 Properties of peat and HA.....	42
2.4.3 Deconvolution of S K-edge XANES spectra .....	45
2.4.4 Normalized and first derivatives of normalized As K-edge XANES spectra .....	46
2.4.5 Shell fits of As K-edge EXAFS spectra of reference compounds.....	47

2.5	References .....	49
<b>3</b>	<b>Arsenite binding to sulfhydryl groups in the absence and presence of ferrihydrite:</b>	
	<b>A model study</b> .....	<b>55</b>
3.1	Introduction .....	56
3.2	Materials and methods.....	57
	3.2.1 Organic and mineral sorbents.....	57
	3.2.2 Arsenite sorption experiments.....	58
	3.2.3 Competitive sorption experiments.....	58
	3.2.4 Oxidation experiment.....	59
	3.2.5 X-ray absorption spectroscopy .....	59
	3.2.6 Surface complexation modeling.....	60
3.3	Results and discussion .....	61
	3.3.1 Characterization of Ambersep GT74.....	61
	3.3.2 Arsenite binding to Ambersep GT74 .....	61
	3.3.3 Surface complexation modeling.....	65
	3.3.4 Competitive sorption experiment .....	66
	3.3.5 Oxidation experiment.....	68
	3.3.6 Environmental implications .....	69
3.4	Supporting information .....	71
	3.4.1 X-ray diffraction pattern of ferrihydrite .....	71
	3.4.2 Time-resolved arsenite binding to Ambersep GT74 .....	71
	3.4.3 Microscopic images of Ambersep GT74 .....	72
	3.4.4 Spectroscopic properties of Ambersep GT74 .....	72
	3.4.5 Alternative surface complexation model for Ambersep GT74.....	75
3.5	References .....	76
<b>4</b>	<b>Arsenite binding to natural organic matter: Spectroscopic evidence for ligand exchange and ternary complex formation</b> .....	<b>81</b>
4.1	Introduction .....	82
4.2	Materials and methods.....	84
	4.2.1 Natural organic matter .....	84
	4.2.2 Reaction of peat with iron and arsenic .....	84
	4.2.3 X-ray diffraction analysis .....	85
	4.2.4 Electron paramagnetic resonance spectroscopy.....	85
	4.2.5 X-ray absorption spectroscopy .....	85
4.3	Results and discussion .....	86

4.3.1 X-ray diffraction and EPR spectroscopy .....	86
4.3.2 Iron X-ray absorption spectroscopy .....	88
4.3.3 Arsenite sorption.....	93
4.3.4 Arsenic X-ray absorption spectroscopy.....	95
4.3.5 Environmental implications .....	99
4.4 Supporting information .....	101
4.4.1 Influence of temperature on Fe K-edge EXAFS spectra of peat .....	101
4.4.2 First derivatives of normalized Fe K-edge XANES spectra .....	101
4.4.3 Shell fits of Fe K-edge EXAFS spectra of reference compounds .....	102
4.4.4 F-statistics of Fe K-edge EXAFS shell fit models of peat samples .....	103
4.4.5 First derivatives of normalized As K-edge XANES spectra .....	104
4.4.6 Shell fit of the As K-edge EXAFS spectrum of As(III) sorbed to ferrihydrite.....	104
4.4.7 Derivation of the As K-edge EXAFS shell fit model .....	106
4.4.8 F-statistics of the validity of the As-C single scattering path .....	107
4.5 References .....	108
<b>5 Conclusions</b> .....	<b>113</b>
5.1 Mechanistic insights into the binding of arsenite to natural organic matter.....	113
5.2 Significance in environmental and technical systems .....	115
5.3 Future research needs .....	117
5.4 References .....	118
<b>Danksagung</b> .....	<b>121</b>
<b>Curriculum Vitae</b> .....	<b>123</b>