

Natürliche Bildung von halogenierten Essigsäuren und Iodalkanen



Isabelle Jasmine Fahimi

Dissertation

Universität Heidelberg

2003

Inaugural – Dissertation

zur

Erlangung der Doktorwürde

der

Naturwissenschaftlich-Mathematischen Gesamtfakultät

der

Ruprecht – Karls - Universität

Heidelberg

vorgelegt von

Isabelle Jasmine Fahimi

aus Boston, Massachusetts, USA

Diplom-Mineralogin, Universität Heidelberg

Master of Environmental Studies, Yale University

2003

Thema:

**Natürliche Bildung von halogenierten Essigsäuren
und Iodalkanen**

Gutachter: Prof. Dr. Heinz Friedrich Schöler

Prof. Dr. German Müller

Promotionsdatum: 27. März 2003

It is a great pleasure to thank Prof. H.F. Schöler for his guidance and constant support during the entire course of this research project

I went to the woods because I wished to live deliberately, in front of the essential facts of life, and see if I could not learn what it had to teach.

from "*Walden*" by Henry David Thoreau

I truly admire Henry David Thoreau (1817 - 1862). He was an American poet who lived in Concord, Massachusetts, and loved nature. He led a simple life, enjoying the wonders of nature. He lived completely isolated for two years, in a small wooden cabin, in midst of the wilderness, on the shores of the Walden Pond near Boston where he wrote his famous book *Walden*. I actually grew up close to where he once had his cabin. We, who research natural processes, we are also sometimes surprised and in awe for what nature has in store for us. Halogenation processes and the formation of hydroxyl radicals in soils are important chemical reactions which may contribute to the diversity and beauty of nature.

ABSTRACT

This thesis deals with organohalogen compounds and their formation by natural abiotic soil processes, providing a framework in which a literature survey and a resume of the multitude of laboratory experiments are integrated.

In the first chapter the literature on the sources, occurrence and sinks of halogenated acetic acids (HAAs), which are phytotoxic, and probably related to forest dieback, is summarized. They are ubiquitous in precipitations and are accumulated in coniferous needles. Next to anthropogenic sources there have also been indications of a natural biotic formation of HAAs in soil.

In the following main segment experiments on the abiotic formation of HAAs in soils are presented. This process is probably due to a coupled oxidation/halogenation of organic matter. Experiments with soils, humic acid and phenolic model compounds show that HAAs are generated abiotically. In the case of ethoxyphenol, this occurs through the oxidation of a C₂-unit, and in the case of the other model substances probably through the breakdown of the aromatic ring system. More dichloroacetic acid (DCA) than trichloroacetic acid (TCA) is formed. The addition of iron and H₂O₂ leads to a further increase in formation of HAAs. Probably a Fenton reaction ($\text{Fe(II)} + \text{H}_2\text{O}_2 \rightarrow \text{Fe(III)} + \text{OH}\cdot + \text{OH}\cdot$) occurs between the iron and the H₂O₂, forming OH radicals which oxidize the Cl⁻, leading to the chlorination of organic matter.

In the fourth chapter the formation of OH radicals, measured by the 2-deoxy-D-ribose method, in aquatic systems with humic acid or soil is investigated; neither sunlight, nor the addition of H₂O₂ or iron is required. The *in vitro* formation of OH radicals increases linearly with the amount of soil or humic acid employed.

In the fifth chapter the abiotic formation of alkyl iodides in soil is studied. Soils, humic acid and model substances were employed. Similar to the formation of HAAs, two reaction pathways are possible: either, in the case of guaiacol, the splitting off of a methyl group and/or the fragmentation of an aromatic system. Probably an oxidation of organic matter with iron is induced. An addition of iron leads to an increase of the production of homologous alkyl iodides from C₁ to C₄; this confirms the redox-induced mechanism of this reaction.

In summary the results of this study indicate that organohalogen compounds are produced abiotically in soil. Their formation is dependent on environmental conditions, e.g. iron content, pH and organic carbon (C_{org}).

ZUSAMMENFASSUNG

Diese Arbeit befasst sich mit Organohalogenverbindungen und deren Bildung bei abiotischen natürlichen Bodenprozessen. Sie enthält eine ausführliche Literaturzusammenfassung und eine Darstellung von Laborversuchen, welche die abiotische Bildung dieser Verbindungen belegen.

Im ersten Kapitel wird die Literatur über Vorkommen, Quellen, und Senken von halogenierten Essigsäuren (HAAs), die phytotoxisch sind und mit dem Waldsterben in Beziehung gebracht werden, zusammengefasst. HAAs kommen ubiquitär in Niederschlägen vor und werden in Koniferennadeln angereichert. Neben anthropogenen Quellen gibt es auch Hinweise auf eine natürliche biotische Bildung von HAAs im Boden.

Im folgenden Hauptabschnitt wird experimentell die abiotische Bildung von HAAs im Boden untersucht. Sie entstehen wahrscheinlich durch eine gekoppelte Oxidation/Halogenierung von organischem Material. Der Einfluss von Boden, Huminsäure und phenolischen Modellsubstanzen wurde experimentell untersucht. Wenn Ethoxyphenol zugegeben wird, bilden sich die HAAs wahrscheinlich durch die Oxidation der C₂-Einheit, und mit den anderen Modellsubstanzen möglicherweise über eine Aufspaltung des aromatischen Rings. Dabei wird mehr Dichloressigsäure (DCA) als Trichloressigsäure (TCA) gebildet. Die HAA-Bildung wird begünstigt, wenn Eisen und H₂O₂ zugegeben werden. Wahrscheinlich findet zwischen dem Eisen und dem H₂O₂ eine Fentonreaktion ($\text{Fe(II)} + \text{H}_2\text{O}_2 \rightarrow \text{Fe(III)} + \text{OH}\cdot + \text{OH}^-$) statt, bei der OH-Radikale entstehen, die Cl⁻ oxidieren können, was zu einer Chlorierung von organischem Material führt.

Im vierten Kapitel wird die Bildung von OH-Radikalen, die mit der 2-Deoxy-D-Ribose Methode nachgewiesen werden, in aquatischen Systemen mit Huminstoffen/Böden untersucht; weder Sonnenlicht, noch H₂O₂ oder Fe werden dafür benötigt. Die *in vitro* Bildung von OH-Radikalen erhöht sich linear mit der Menge an Boden/Huminsäure, die eingesetzt wird.

Im fünften Kapitel wird die abiotische Bildung von iodierten Alkanen untersucht. Die Oxidation der organischen Substanz des Bodens wird mit Eisen induziert. Böden, Huminsäure und Modellsubstanzen wurden experimentell untersucht und es wurden Hinweise, auf zwei mögliche Reaktionsmechanismen gefunden: einmal, im Fall von Guajakol, durch die Abspaltung der Methylgruppe, und zweitens durch eine Aufspaltung des aromatischen Rings. Eine Zugabe von Eisen führte zu einer

Erhöhung der Bindung von den homologen Iodalkanen von C₁ zu C₄, was den redox-induzierten Mechanismus bestätigt.

Organohalogenverbindungen können abiotisch im Boden gebildet werden, ihre Produktion ist von den Umweltbedingungen, z.B. Eisengehalt, pH, und organischen Kohlenstoffgehalt (C_{org}) des Bodens abhängig.

TABLE OF CONTENTS

1	INTRODUCTION: HALOGENATED ACETIC ACIDS (HAAS)	1
1.1	PROPERTIES OF CHLORINATED ACETIC ACIDS (CAAs).....	1
1.2	SOURCES	2
1.2.1	<i>Usage of chlorinated acetic acids as herbicides</i>	2
1.2.2	<i>Sources of HAAs in the atmosphere</i>	2
1.2.2.1	Photochemical degradation of C ₂ -chlorocarbons	4
1.2.2.2	Formation of TCA from tetrachloroethene	4
1.2.2.3	Formation of TCA from 1,1,1-trichloroethane	6
1.2.2.4	Formation of DCA from trichloroethene	8
1.2.2.5	Formation of TCA from TRI and PER vs. actual environmental levels	9
1.2.2.6	Reaction of Cl radicals with atmospheric organic matter	9
1.2.3	<i>Other sources of chlorinated acetic acids</i>	10
1.2.4	<i>Natural production of TCA in soil</i>	10
1.3	OCCURRENCE OF CHLORINATED ACETIC ACIDS IN THE ENVIRONMENT.....	12
1.3.1	<i>Hydrosphere</i>	12
1.3.1.1	Precipitation	12
1.3.1.2	Throughfall.....	16
1.3.1.3	Firn and snow.....	16
1.3.1.4	Fog.....	18
1.3.1.5	Sewage waters	18
1.3.1.6	Seawater	18
1.3.1.7	Peat bog waters	19
1.3.1.8	Lakes and rivers	19
1.3.1.9	Groundwater	20
1.3.2	<i>Air</i>	21
1.3.3	<i>Biosphere</i>	22
1.3.3.1	Concentrations of TCA in needles and leaves.....	22
1.3.3.2	Age-dependency and seasonal dependence of TCA in needles	23
1.3.3.3	Influence of kraft pulp mills on TCA concentrations of conifer needles	24
1.3.3.4	Conversion of precursors in the plant	25
1.3.3.5	CAAs in vegetables, fruit, grain and tobacco.....	26
1.3.3.6	Physiological effects of TCA on plants.....	26
1.3.3.7	Phytotoxicity of CAAs.....	28
1.3.3.8	TCA and forest decline.....	30
1.3.3.9	Animal tissue.....	31
1.3.4	<i>Soil</i>	31

1.4	REMOVAL PROCESSES.....	34
1.4.1	<i>Removal processes from soil</i>	34
1.4.2	<i>Uptake of TCA into plants</i>	36
1.4.3	<i>Degradation of TCA in plants</i>	38
1.4.4	<i>Removal processes from water</i>	38
1.4.5	<i>Removal processes of TCA in air</i>	38
1.5	HAAs IN THE CONTEXT OF OTHER HALOGENATED SUBSTANCES.....	39
1.6	IODINATED ALKANES	39
2	RESEARCH OBJECTIVES	42
3	CAA FORMATION STUDIES IN SOIL AND ENVIRONMENTAL SAMPLES	43
3.1	SUMMARY.....	43
3.2	EXPERIMENTAL SECTION.....	43
3.2.1	<i>Materials</i>	43
3.2.2	<i>Synthesis of diazomethane</i>	44
3.2.3	<i>Method: Extraction, volume reduction and derivatization: humic acid and model substance experiments, environmental samples</i>	45
3.2.4	<i>Gas chromatography</i>	45
3.3	RESULTS AND DISCUSSION	47
3.3.1	<i>Soil and Fluka humic acid suspended in water form CAAs</i>	48
3.3.2	<i>Influence of H₂O₂, Fe(III) and Fe(II) on formation of chloroacetic acid</i>	51
3.3.3	<i>Model substances: moieties of humic acids form HAAs</i>	53
3.4	CONCLUSIONS.....	57
4	OH RADICAL FORMATION IN SOIL.....	59
4.1	SUMMARY.....	59
4.2	INTRODUCTION.....	59
4.3	EXPERIMENTAL SECTION.....	61
4.3.1	<i>Materials</i>	61
4.3.2	<i>2-Deoxy-D-ribose method</i>	62
4.3.2.1	<i>Principle of the 2-DR method</i>	62
4.3.2.2	<i>Procedure</i>	63
4.3.3	<i>Influence of iron</i>	65

4.4	RESULTS AND DISCUSSION	66
4.4.1	<i>Influence of humic acid content on the OH radical formation.....</i>	66
4.4.2	<i>Influence of pH on OH radical formation.....</i>	69
4.4.3	<i>Time dependence of OH radical formation</i>	69
4.4.4	<i>Influence of oxygen on the OH radical formation.....</i>	70
4.4.5	<i>Estimation of the OH radical concentration in the solution</i>	73
5	FORMATION OF VOLATILE IODINATED ALKANES IN SOIL.....	75
5.1	SUMMARY.....	75
5.2	INTRODUCTION.....	75
5.3	EXPERIMENTAL SECTION	78
5.3.1	<i>Materials.....</i>	78
5.3.2	<i>Procedure.....</i>	79
5.3.3	<i>Analysis.....</i>	79
5.4	RESULTS AND DISCUSSION	81
5.4.1	<i>Soil-water experiments: without additives.....</i>	81
5.4.2	<i>Influence of Fe(III) and iodide.....</i>	83
5.4.3	<i>Influence of pH.....</i>	86
5.4.4	<i>Proposed reaction schemes.....</i>	87
5.5	CONCLUSIONS	88
6	SUMMARY.....	90
7	REFERENCES.....	95

LIST OF ABBREVIATIONS

A _h	A-horizon
AOX	adsorbable organic halogen
B _h	B-horizon
CAAs	chlorinated acetic acids
C _{org}	organic carbon
CPO	chloroperoxidase
2,4-D	2,4-dichlorophenoxyacetic acid
DCA	dichloroacetic acid
DCAC	dichloroacetyl chloride
DMSO	dimethyl sulfoxide
2-DR	2-deoxy-D-ribose
ECD	electron capture detector
ESR	electron spin resonance
FAO	United Nations Food and Agricultural Organization
GC	gas chromatograph
GST	glutathionine S-transferase
HAAs	halogenated acetic acids
HA	humic acid
HQ	hydroquinone
HS	humic substance
ID	inner diameter
INAA	instrumental neutron activation analysis
L.O.D.	limit of detection
MCA	monochloroacetic acid
MS	mass spectrometer
O _h	O-horizon
PEC	predicted environmental concentration
PER	tetrachloroethene
PNEC	predicted no effect concentration
POX	peroxidase
ppm	parts per million (corresponds to mg/l)
RSD	relative standard deviation
SQ	semiquinone
2,4,5-T	2,4,5-trichlorophenoxyacetic acid
TCA	trichloroacetic acid
TCAC	trichloroacetyl chloride
1,1,1-TCE	1,1,1-trichloroethane
TBA	thiobarbituric acid
TRI	1,1,2-trichloroethene
VHOC	volatile halogenated organic compounds
VIOC	volatile iodinated organic compounds

