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含む。）
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なし。
2. 実用新案登録
なし。
3. その他
なし。

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研究成果の刊行物・別刷

湖沼における
難分解性溶存有機物の蓄積

今井 章雄

1. はじめに

近年，多くの湖沼において，流域発生源対策が行われているにもかかわらず，難分解性と考えられる溶存有機物 (DOM, dissolved organic matter) が徐々に増え続けている。今まで想定されていなかったタイプの水質汚濁現象が起きている。湖沼環境保全上，早急に，この新しい有機汚濁現象のメカニズムを解明することが求められている。本小論では，現時点での湖沼難分解性 DOM に対する認識・理解を述べ，続いて著者らの研究，すなわち，湖水中の DOM がどのような性質を持ち，どのような影響を及ぼすか，また，どのような対策が必要か等について記述する。

(a) 難分解性溶存有機物が最初に注目されたのは？

湖沼における難分解性 DOM が最初に注目されたのは 1980 年代後半，わが国最大の湖，琵琶湖の北湖においてである[1]。琵琶湖北湖における生物化学的酸素要求量 (BOD, biochemical oxygen demand) と化学的酸素要求量 (COD, chemical oxygen demand) の経年変化を図 1 に示す。BOD は容易に分解する (易分解性) 有機物量を，COD は有機物の全量を表す。ともに有機物を酸素当量として表したものである。図から明らかに，琵琶湖湖水中の COD 濃度は 1984 年を境に徐々に増加している。ところが，易分解性有機物量を表す BOD は横這い，あるいは低減傾向にある。加えて，湖水 COD のほとんどは溶存態からなる。まとめると，琵琶湖北湖の湖水中では，易分解性ではない，すなわち難分解性で溶存態の有機物，難分解

性 DOM が徐々に蓄積していると言える。植物プランクトンの量を示すクロロフィル-a は増加しておらず，また長年にわたる発生源対策により湖沼流域から入ってくる有機汚濁物量も増えているとは考えられない。すなわち，何らかの新しいタイプの水質汚濁現象が起こっている。湖沼環境保全対策の観点から視ると，とても困ってしまう状況にある。

(b) 最近のトレンドは？

琵琶湖で観察された溶存態 COD の漸増現象は，その後，遍在的な広がりをみせている。同様な濃度上昇が，霞ヶ浦，印旛沼，十和田湖，野尻湖，そして内湾海域である富山湾でも報告されている。すべてのケースで共通するのは，冬季にこれまで減少していた COD 濃度が減少せずに増加に転じたことである。湖沼はその栄養塩 (窒素，リン) 濃度や植物プランクトン量で分類される。植物プランクトン密度や栄養塩濃度の高い霞ヶ浦や印旛沼は富栄養湖，琵琶湖は中栄養湖，十和田湖や野尻湖は貧栄養湖に該当する。つまり，湖の栄養状態にかかわらず，また，湖と海域
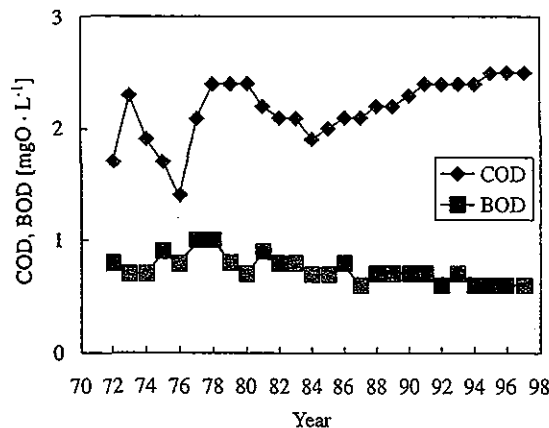
図 1　琵琶湖北湖における化学的酸素要求量 (COD) と生物化学的酸素要求量 (BOD) の経年変化。

の違いにも関係なく, 溶存態 COD が漸増している訳である。それも, 顕著な濃度上昇は同一季節に起きている。この漸増する溶存態 COD, すなわち難分解性 DOM の原因が人間活動に由来したものであると推論しても, あながち穿った見方とは言えないだろう。

(c)難分解性 DOM の漸増によって起こる環境問題

湖水中の難分解性 DOM 濃度が上昇すると, 以下の諸問題が顕在化すると考えられる。(1)環境基準達成の困難：湖沼の環境基準は COD で規定されており, COD 濃度の漸増は環境基準の達成を難しいものとする。(2)流域発生源対策のあり方：湖沼流域発生源対策が行われているのに湖水 COD 濃度が漸増している。既存の発生源対策の有効性に疑問符が打たれる。(3)湖沼生態系への影響：DOM は湖沼の植物プランクトンの増殖や種組成に大きな影響を及ぼすと報告されている。難分解性 DOM の漸増は新しいタイプの水質汚濁現象であり, 湖沼生態系に及ぼす影響が懸念される。(4)有害化学物質の可溶化：DOM は重金属や農薬等の有害化学物質と結合し可溶化させることが知られている。DOM 濃度上昇による有害化学物質の能動化が懸念される。(5)水道水源水としての問題：水道水源としての湖沼に着目すると, DOM は浄水処理過程の塩素殺菌プロセスにおいて生成される発ガン物質トリハロメタン等の前駆物質とみなせる。DOM 濃度上昇に伴うトリハロメタン等の消毒副生成物による健康リスクの上昇が懸念される。

2. 難分解性溶存有機物の特性と起源

(a)DOM 分画分布特性

現時点で, 湖水中の難分解性 DOM がなぜ増えるのか, そのメカニズムについてはよくわかっていない。これは, DOM が複雑で不均質な混合体であり, 天然水中の DOM に関しては過去 20 年間に渡り精力的に研究が行われてきたにもかかわらず, 依然としてその中味が不明瞭なためである。このような状況では, 研究の第 1 歩は DOM の特性把握にならざるを得ない。われわれの選択したアプローチは, 可能な限り明白な切り口で DOM をマクロ的に分画して, 各画分の分布および特性を評価することであった。このマクロ分画の基礎となる物質として溶存フミン物質(aquatic humic substances)を選択した。フミン物質は疎水性の有機酸で, 天然水中の DOM の 30 〜 80％を占める典型的な難分解性 DOM である。一般

に土壌有機物, 陸上・水生植物やプランクトン由来と言われ, 湖水に流入する主要な外来性 DOM と考えられる。湖水中の難分解性 DOM を分画する際に, 分離・分画の基礎となる参照物質として適切なものと言える。

フミン物質は, 難分解性で疎水性の有機酸である。すなわち, DOM 分画の切り口は, 易分解性ー難分解性, 疎水性ー親水性, 酸性ー塩基性となる。この三つの切り口を使い, フミン物質の分離に基礎をおく, DOM 分画手法を開発した(図 2)[2]。この分画手法は, 長期間(100 日間)生分解試験(易分解性ー難分解性)と樹脂吸着分画手法(疎水性ー親水性, 酸性ー塩基性)からなる。分画後に各画分の物理化学的パラメータ(溶存有機炭素[DOC, dissolved organic carbon], 紫外部吸光度特性, 分子量分布等)を測定することにより DOM の特性を評価した。樹脂吸着分画法は 3 種類の樹脂(非イオン性, 陽イオン交換, 陰イオン交換樹脂)を用いて DOM を 5 つに分画する：フミン物質, 疎水性中性物質, 親水性酸, 塩基物質(≒親水性塩基物質), 親水性中性物質。
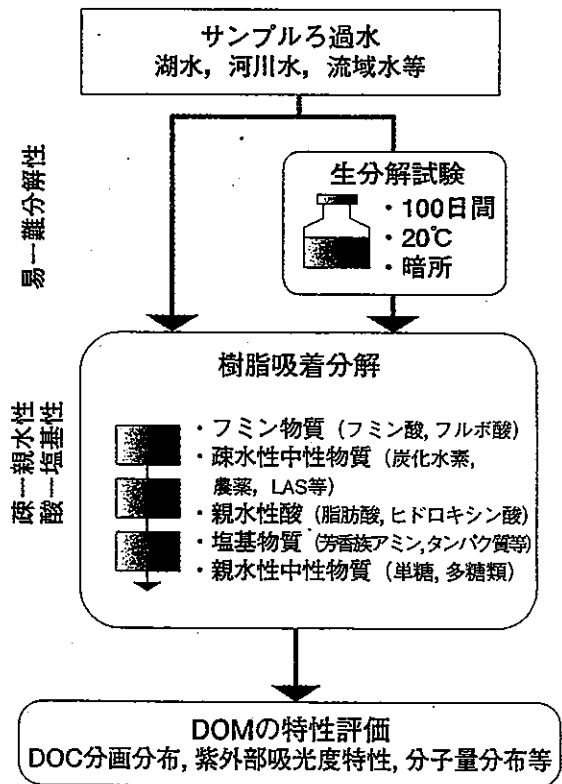

図2　溶存有機物(DOM)分画手法の概要。
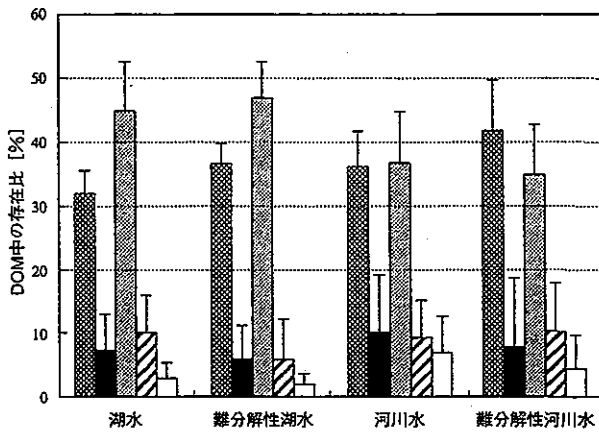
図3 霞ヶ浦湖水および流入河川水の溶存有機物(DOM)分画分布。

図4 霞ヶ浦湖心における溶存有機物(DOM)，フミン物質，親水性酸および難分解性DOM，フミン物質，親水性酸の動態(1997年)。

　この DOM 分画手法を，わが国で2番目に大きな湖で，典型的な富栄養湖である霞ヶ浦の湖水および流入河川水に適用した。得られたDOM分画分布を図3に示す[3]。霞ヶ浦湖水ではDOM成分としては有機酸，すなわちフミン物質と親水性酸が卓越していた。この2つの画分がDOMの70%以上を占めており，特に親水性酸の寄与が大きかった。河川水中のDOM分画分布は湖水と大きく異なっていた。湖水と同様にフミン物質と親水性酸が優占していたが，フミン物質と親水性酸の存在率はほぼ同程度であった。難分解性DOMの分画分布においても，湖水と河川水ともにフミン物質と親水性酸が難分解性DOMの大部分を占めていた。河川水では従来報告されているようにフミン物質が多かったが，湖水では親水性酸のほうが圧倒的に優占していた。この関係は琵琶湖北湖や諏訪湖の湖水にもあてはまる。すなわち，こと湖水に限っては，一般に言われているフミン物質ではなく，もっと親水性の有機酸が難分解性DOMとして重要と言える。

　霞ヶ浦流域内の様々なDOM発生源水サンプル(田んぼ流出水，森林渓流水，生活雑排水，下水処理水，アオコを形成するラン藻類の培養後ろ液等)を採取しDOM分画手法を適用した。得られたDOM分画分布(生分解試験前)はサンプルの起源により顕著に異なっていた。湖水のDOM分画分布がどのサンプルのそれに類似しているかを検討するために，分画分布データを用いてクラスター解析を行ったところ，湖水と最も類似するサンプルは下水処理水であった。
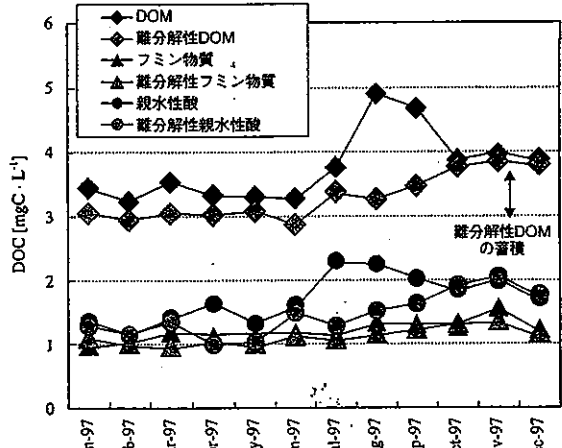
　また，DOM分画分布データおよび紫外部吸光度：DOC(UV：DOC)比データを用いて段階的2分割という手法でサンプルの類別化を行ったところ，霞ヶ浦湖水と下水処理水を有意に分割することができなかった。これは先のクラスター解析の結果と一致する。すなわち，霞ヶ浦湖水は下水処理水に似た水なのかもしれない。

　(b)DOM および難分解性 DOM の動態
　霞ヶ浦湖水における1997年のDOM，フミン物質，親水性酸および難分解性DOM，フミン物質，親水性酸の動態を図4に表す。DOMと親水性酸の分解率は夏期に最大となるが，冬期には極めて低い値を示した。夏期の大きな分解率は，この期間に植物プランクトン由来で易分解性の親水性酸が生産されたことを示している。フミン物質は1年を通じて極めて難分解性であった。フミン物質が難分解性であることは予想通りであったが，親水性酸も極めて難分解性であることは新しい発見であった。単純にみると，1997年には1年間で難分解性DOMが約0.8 mgC・L⁻¹増えている。この期間，難分解性フミン物質は約0.2 mgC・L⁻¹，難分解性親水性酸は約0.8 mgC・L⁻¹上昇した。したがって，湖水中の難分解性DOMの増大は，主に難分解性親水性酸の増大，特に秋から冬にかけての増大によるものと言える。

　難分解性DOMの秋から冬にかけての増大パターンは，湖における一般的なDOMの季節変化パターンとは考えられない。霞ヶ浦に流入する河川水の流量およびDOM濃度(DOCとして)は秋から冬に顕著

に低下する。このため，通常，冬から春先にかけて河川水由来のDOM負荷は年間を通して最も低くなる。冬期に難分解性DOMが最大になる現象は，少なくとも河川水由来DOMによって引き起こされたものではないと言える。霞ヶ浦の場合，湖畔に流域下水処理場があり，処理水を直接湖に放流している。この処理場の放流水量は年間を通してほぼ一定で約50,000 $m^3 \cdot d^{-1}$であり，夏から冬の河川水量の13%に相当する。下水処理水のDOM濃度は河川水よりも高いため，そのDOMとしての寄与は水量比較よりも高くなる。つまり，下水処理水の湖水難分解性DOMへの寄与は無視できないほど大きいことになる。

　ここで興味深いのは，琵琶湖，霞ヶ浦，十和田湖等でCOD濃度が漸増する要因として，冬季にCOD濃度が例年通りに減少しないことが挙げられていることである。つまり，霞ヶ浦における1997年の難分解性DOM濃度の冬季における蓄積は，いわゆるCODの漸増現象と整合する。

3．難分解性溶存有機物の及ぼす影響

　(a)水道水源として湖沼水質（トリハロメタン生成能）

　湖沼を水道水源として捉えると，DOMは浄水処理過程で生成されるトリハロメタン等の前駆物質であるため，湖水中のDOMおよび難分解性DOM濃度の上昇は水道水源保全の観点からとても由々しき問題と言える。

　わが国における浄水塩素殺菌処理による発ガン物質トリハロメタン生成に関する研究は，1970年代から1980年代初めにかけて盛んに行われた。その成果として，トリハロメタンの主要な前駆物質はフミン物質であると報告されている。ところが，本研究でも実施している天然水中からの溶存態フミン物質の分離・抽出方法が，米国地質調査所の研究者らによって開発・確立されたのは1980年代中頃である。この時間のズレは，わが国でトリハロメタン研究が精力的に行われた時期に，フミン物質の分離手法が存在しなかったことを意味する。実際に，トリハロメタン生成に関する研究において，湖沼・河川水からフミン物質を分離・抽出し，フミン物質のトリハロメタン生成能を測定したとする報告例は皆無である。すなわち，実際に湖水からフミン物質を分離して，そのトリハロメタン生成能を測定してみると，新しい知見が得られる可能性が高い。
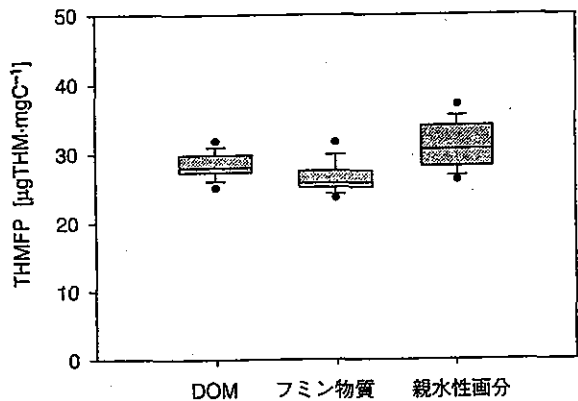
　図5に，霞ヶ浦浄水処理場の取水地点に近いポイ

図5　霞ヶ浦湖水中の溶存有機物(DOM)，フミン物質，親水性画分のトリハロメタン生成能(THMFP)。
親水性画分＝親水性酸＋塩基物質＋親水性中性物質。
THMFP = $CHCl_3$ + $CHCl_2Br$ + $CHClBr_2$ + $CHBr_3$。

ントで採取した湖水サンプルのろ過湖水(DOM)，フミン物質および親水性画分(＝[親水性酸]＋[塩基物質]＋[親水性中性物質])のトリハロメタン生成能(THMFP, trihalomethane formation potential = $[CHCl_3]$＋$[CHCl_2Br]$＋$[CHClBr_2]$＋$[CHBr_3]$)の測定結果を示す[2]。この採取地点での1997年におけるDOM，フミン物質，親水性画分の平均トリハロメタン生成能は，それぞれ28.4, 26.9, 31.4 $\mu gTHM \cdot mgC^{-1}$であった。親水性画分のトリハロメタン生成能はフミン物質よりも有意に大きかった($P < 0.01$)。霞ヶ浦では親水性画分のほうがフミン物質よりも約2倍濃度が高いことを考えると，明らかに，トリハロメタン前駆物質として親水性画分のほうがフミン物質よりも重要であると結論される。さらに，DOMおよび難分解性DOMの濃度上昇には，フミン物質よりも非フミン物質である親水性酸の寄与が大きいことを考えると，湖沼で観察されている難分解性DOMの漸増現象は，水道水源水としての湖水のトリハロメタン生成能に係わる健康リスクの増大に直接的に関与すると推察される。

　(b)植物プランクトン種組成

　湖沼でアオコを形成するラン藻類は，光合成，亜硝酸および硝酸還元，クロロフィル合成等の生理機能を維持するために鉄を必須とし，その要求量は他の藻類に比較して大きい。

　典型的な難分解性DOMであるフミン物質は金属イオンと安定した錯体を形成し，一般的に鉄に対する錯化能は大きい。フミン物質の植物プランクトン

増殖に及ぼす影響については，増殖を促進したとするものと増殖を抑制したとするもの，相反する報告がなされている。いずれにせよ，フミン物質の存在は植物プランクトンの増殖に大きな影響を及ぼすだろうと推察される。

DOM 分画実験の結果等を見ると，霞ヶ浦における難分解性 DOM 濃度の上昇は，フミン物質ではなく，主に難分解性親水性酸によるものと示唆される。ただ，霞ヶ浦の場合，フミン物質濃度が他の湖沼に比べてかなり高い。富栄養湖である霞ヶ浦のフミン物質濃度が $0.97 \sim 1.57$ mgC·L^{-1} なのに対して，中栄養湖の琵琶湖北湖で $0.37 \sim 0.41$ mgC·L^{-1}，アオコが毎夏発生する諏訪湖で 0.5 mgC·L^{-1} 程度である。したがって，霞ヶ浦における高いフミン物質濃度は，鉄との錯化反応を介して，ラン藻類の増殖や種組成に大きな影響を及ぼすと推測される。

この仮説を検証するために，藻類増殖用培地（CB培地）に霞ヶ浦から分離・精製したフミン物質を添加してラン藻の増殖実験を行った。供試ラン藻類としては霞ヶ浦湖水より分離されたアオコを形成するラン藻類 Microcysitis aeruginosa を用いた。結果，霞ヶ浦湖水から分離したフミン物質は，M. aeruginosa の増殖を著しく抑制することが明らかとなった（図6）[4]。注目すべきは，霞ヶ浦湖水中のフミン物質濃度に匹敵する濃度レベルでも高い抑制作用があることである（フミン物質 2 mgDW·$L^{-1} \fallingdotseq 1$ mgC·L^{-1}）。化学平衡モデル（MINEQL）を用いた計算によれば，現在の霞ヶ浦湖水では，フミン物質の錯化反応により，M. aeruginosa は過酷な鉄不足状態にあるため増殖できないと推察された。

富栄養湖である霞ヶ浦では，Microcystis 属（そのほとんどは Microcystis aeruginosa）による異常増殖（アオコ）が 1986 年まで毎年観察されていた。しかし，翌 1987 年を境として Microcystis によるアオコは突然姿を消した。このときから Microcystis が減少し，代わりに Oscillatoria 属等の糸状ラン藻が優占するという，ラン藻類の種組成に大きな変化が起きた。湖内の窒素とリンの比（N／P比）が高くなり，窒素制限からリン制限に変わったため Microcystis から糸状ラン藻類へ優占種が遷移したという説が提唱された。しかし，現在，湖水のN／P比はリン濃度の上昇に伴い 1987 年以前の N／P 比に近い値になっているが，Microcystis は優占種に戻っておらず，なぜ優占ラン藻類の種組成が変化したか明白にわかっていない。
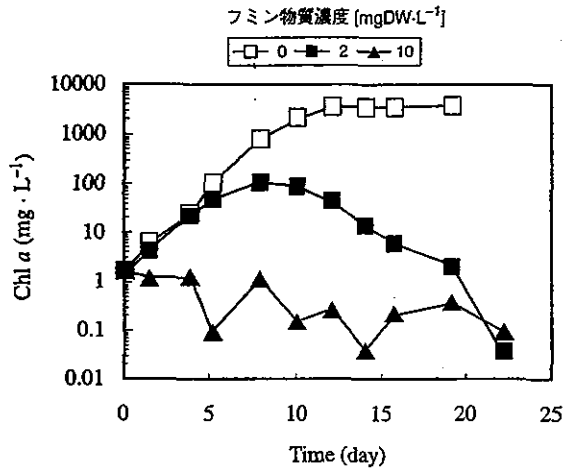
フミン物質濃度 [mgDW·L^{-1}]

図6 フミン物質の Microcystis aeruginosa の増殖に及ぼす影響。
添加フミン物質はフルボ酸；溶存 Fe 濃度：$10^{-5.56}$M；DW：乾燥重量；フルボ酸の有機炭素含量：54.0%。

われわれの得た知見，すなわち，「現在の霞ヶ浦では Mircrocystis aeruginosa は鉄不足で増殖できない」という示唆は，Microcystis 属が霞ヶ浦で優占種でなくなった事実と符合する。ただし，1986 年以前のフミン物質濃度や溶存鉄濃度に関するデータがなく，フミン物質濃度が上昇したため Microcystis が減少したとは明言できない。

4. 有機汚濁発生源対策の落とし穴

湖水中の溶存態 COD 濃度が徐々に増えているという現象から，難分解性 DOM が湖水中で増えているのだと推察しているわけであるが，この推察には大きな落とし穴がある。わが国の湖沼有機物指標（環境基準）である COD は過マンガン酸カリウム法による COD（CODMn）である。しかし，CODMn には，（1）河川の基準項目である BOD と異なる，（2）酸化率が低く，また物質によって収率が異なることから有機物の総量を表す指標となっていない，（3）希釈の程度により分析結果が異なる，（4）酸化の程度が温度，反応時間の影響を受けやすいので測定値のバラツキが大きい，といった問題点がある[5]。すなわち，CODMn は加算性がない（1＋1≠2）。この理由により，欧米では重クロム酸カリウム法による COD（CODCr）が標準的で国際規格に採用されている。つまり，厳密な意味では，湖沼における COD 濃度の漸増現象が DOM 濃度上昇によるものか，DOM の質の変化によるものか区別がつかないことになる。

湖沼における流域発生源対策は暗黙のうちに**物質**収支に基づいて実施されている。しかし，メインの有機物指標である CODMn では収支がとれないわけである。対策とその効果に合理的な繋がりが無いことを意味する。湖沼での有機物指標 CODMn の抜本的な見直しが必要である。発生源対策をより実効あるものとするために，物質収支の取れる有機物指標（1＋1＝2）を導入すべきである。CODCr はそもそも有害物質である6価クロムを使用するためわが国で採用されなかった経緯を持つ指標である。したがって，内容の意味するものの明確さ，操作性，管理への応用という面で優れている有機炭素（TOC, total organic carbon あるいは DOC）の採用が望まれる。

ここで視点を広げて，湖沼単独ではなく，自然の水循環の中の一つの要素をとして湖沼を見てみよう。湖に流入する河川の有機物指標（環境基準）は BOD だが，BOD は易分解性有機物指標であり全有機物量を表すものとして不適切である。河川の環境基準達成率は年々向上し高い水準にあるが，実際には BOD 濃度は低いにもかかわらず DOM 濃度は高い可能性も大いにある。例えば，水量不足を補うために下水処理水を大量に放流している都市河川では，BOD としての環境基準は達成しているが DOM 濃度自体はかなり高いだろう。海域の有機物環境基準は湖沼の場合と同じく物質収支の取れない CODMn である。この指標を用いて，指定海域の総量規制（物質収支的アプローチ）を実施する意義はあるのだろうか？環境基本計画において，降水→土壌水→地下水→地表水（河

川・湖沼）→海洋という流下過程における健全な水循環の確保が重要であると謳われている。水循環を考察する際に，この水の流下過程をひとつの流域として捉えざるを得ない。流域の各要素は水の流れで繋がっており，流域の健全な水循環の確保を目的とする保全対策に，同一の有機物指標を採用することは自明の理である。

すなわち，湖沼における難分解性 DOM 対策ひいては健全な水循環の確保のためにも，物質収支の取れる統一指標の導入が必要である。過去30年近いデータの膨大な蓄積のある指標を変えることは難しいことであるが，CODMn では不明瞭な対策を遂行し続けることに他ならない。清水の舞台から飛び降りる気持ちで，指標の見直しをする時は，来た！ちなみに COD を反対から読めば DOC（溶存有機炭素）となる。見方を変えれば指標変更も簡単なことかもしれない。

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Abstract: A steady accumulation in recalcitrant dissolved organic matter (DOM) has been observed in several lakes in Japan, even though extensive measures have been implemented in order to reduce organic pollutant loadings from their catchment areas. This phenomenon is apparently new and has not been given any previous consideration. Characteristics of recalcitrant DOM in a shallow eutrophic lake were evaluated using a DOM macro-fractionation method, by which DOM was fractionated into five classes: aquatic humic substances, hydrophobic neutrals, hydrophilic acids, hydrophilic neutrals and bases (≒ hydrophilic bases). DOM-fraction distribution patterns were found significantly different between the lake and its inflowing rivers.

Trihalomethane formation potential of dissolved organic matter in a shallow eutrophic lake

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Abstract

Dissolved organic matter (DOM) in water samples from the shallow eutrophic Lake Kasumigaura, the second largest lake in Japan, was fractionated and characterized by using resin adsorbents into 5 classes: aquatic humic substances (AHS), hydrophobic neutrals, hydrophilic acids (HiA), bases (BaS) and hydrophilic neutrals (HiN). Subsequently, the trihalomethane formation potential (THMFP), ultraviolet absorbance to dissolved organic carbon (UV:DOC) ratio, and molecular size distribution of the DOM, AHS and hydrophilic fractions (HiF) (HiF = HiA + BaS + HiN) were examined. The THMFP of HiF, normalized on a DOC basis, was found to be comparable to that of AHS ($0.176\,\mu mol\,THM\,mg\,C^{-1}$ vs. $0.195\,\mu mol\,THM\,mg\,C^{-1}$, respectively). The importance of HiF over AHS as a THM precursor became more pronounced when THMFP was evaluated in terms of concentration. In this case, the THMFP of HiF was much greater than that of AHS ($0.374\,\mu mol\,THM\,l^{-1}$ vs. $0.229\,\mu mol\,THM\,l^{-1}$, respectively). Molecular size distributions all exhibited a narrow size range and relatively low molecular weights. The weight-averaged molecular weights of DOM, AHS and HiF were 780, 957 and $606\,g\,mol^{-1}$, respectively.
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Keywords: Trihalomethane formation potential; Lake water; DOM; Aquatic humic substances; Hydrophilic fractions; Molecular weight

1. Introduction

Organic matter plays a vital role in the geochemical and ecological processes of aquatic systems [1,2]. Furthermore, dissolved organic matter (DOM) has become increasingly important with regard to water supplies, because it reacts with chlorine during the disinfection process in drinking water treatment and produces disinfection by-products such as trihalomethanes (THMs). The formation of THMs is of much concern because of their carcinogenic effects on humans [3,4]. THMs in drinking water constitute a potential health risk.

Various organic molecules common in the DOM of surface waters act as precursor materials that form THMs during chlorination. Aquatic humic substances (AHS), comprising fulvic and humic acids, are the most common precursors of THMs [5]. Accounting for about half of the DOM in natural water supplies, AHS are straw-colored, polyelectrolytic, refractory, non-volatile hydrophobic organic acids [2]. Numerous laboratory studies have demonstrated that chlorination of AHS, or of model compounds that are components of AHS material, yields the same THMs as those observed in finished drinking water, strongly suggesting that AHS are the major THM precursor in natural water supplies. However, Owen et al. [6] reported that the reactivity of the non-humic (hydrophilic) fraction of DOM with chlorine was comparable to that of the hydrophobic fraction (AHS and hydrophobic-neutral DOM) when THM formation was normalized on a dissolved organic

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carbon (DOC) basis. Furthermore, a recent study on the THM formation potential of AHS showed that AHS may not account for all the THM formation potential of water samples [5]. These findings point to a high possibility that hydrophilic DOM can be a significant THM precursor as well.

Imai et al. [7], modifying the DOM fractionation method developed by Leenheer [8], fractionated DOM in the waters of Lake Biwa, the largest lake in Japan, into 6 classes: hydrophobic acids (equivalent to AHS), neutrals, and bases (BaS); and hydrophilic acids (HiA), BaS, and neutrals. They found that HiA predominated heavily over AHS in the lake water, accounting for 48% of the DOM as DOC vs. 25% for AHS. Imai et al. [9] also found that at the center of the shallow eutrophic Lake Kasumigaura, the second largest lake in Japan, just as at Lake Biwa, HiA were present in a greater concentration as DOC than were AHS (40% vs. 32%). Thus, the question arose as to whether or not non-humic (hydrophilic) DOM such as HiA is a more important THM precursor than AHS when lake water is used as a drinking water supply. This question is worth asking, because in lake water HiA are likely to be dominant over AHS in terms of DOC concentration. Undoubtedly, more work is needed to characterize the non-humic or hydrophilic components of DOM in lake water and their ability to act as THM precursors.

This paper describes determinative comparisons of trihalomethane formation potential (THMFP) between AHS and non-humic (hydrophilic) DOM in a eutrophic lake, Lake Kasumigaura, which is utilized as a drinking water supply. The objectives of this study were (1) to apply a DOM fractionation method to the lake-water samples and evaluate DOM-fraction distribution, ultraviolet-absorption, and molecular size distribution, and (2) to determine the comparative significance of AHS and hydrophilic fractions (HiF) of DOM as THM precursors by measuring their THMFP at a constant precursor concentration, and (3) to examine the relationships between their THMFP and physico-chemical characteristics.

2. Materials and methods

2.1. Collection of water samples

Lake Kasumigaura, the second largest lake in Japan, is located in the eastern part of the Kanto Plain, 50 km northeast of Tokyo. More than 900,000 people live in the lake's watershed (1577 km^2). Land use in the watershed is 30% forest, 25% paddy field, 25% plowed field, 10% residential, and 10% other. The lake basin is smooth and shallow, with a surface area of 171 km^2, a mean depth of 4.0 m, and a maximum depth of 7.3 m. Because of its extremely high loads of organic matter

and nutrients, this lake is well known for eutrophication, with mean concentrations of chlorophyll-a, phosphorus, and nitrogen of 61, 103, and 1.00 mg l^{-1}, respectively, measured at the center of the lake from January 1997 to December 1997 [10]. Lake Kasumigaura is the source of raw drinking water supply for about 660,000 people. A water treatment plant has been installed near the shoreline of the lake, producing about 28×10^4 m^3 d^{-1} of finished drinking water.

We have been conducting numerous basic studies on Lake Kasumigaura over a period of nearly 20 yr [10]. Several sampling points have been fixed for the purpose of the monitoring. In this study, water samples were collected monthly from January 1997 to December 1997 from one monitoring site near the intake of the water treatment plant (36°03′43″N, 140°14′11″E) in a 1-l glass bottle with a 2-m column sampler. The samples were immediately cooled in an ice cooler and brought back to our laboratory. The water was then filtered through a precombusted (450°C for 4 h) Whatman GF/F filter (Whatman Japan Ltd., Tokyo, Japan, nominal pore size 0.7 μm). The filtrate was usually kept at 3°C in a precombusted glass bottle until analysis.

2.2. DOM fractionation

Sample filtrates were fractionated into 5 fractions: AHS, hydrophobic neutrals (HoN), HiA, BaS, and hydrophilic neutrals (HiN), based on their adsorption on a series of macroporous resin adsorbents [7–9]. Non-ionic Amberlite XAD-8 resin (20–60 mesh, Sigma Chemical Co., St. Louis, USA), strong cation-exchange resin (Bio-Rad AG-MP-50, 50–100 mesh, Nippon Bio-Rad Lab. KK, Tokyo, Japan), and strong anion-exchange resin (Bio-Rad AG-MP-1, 50–100 mesh) were used.

The XAD-resin was cleaned and conditioned as described by Thurman and Malcolm [11]. Three milli-liters (wet volume) of the XAD-8 resin was packed into a glass column and rinsed 3 times, alternating 0.1 M NaOH with 0.1 M HCl each time, just before application of the sample. A blank sample was collected from the final rinse with 0.1 M HCl (B1). Both the AG-MP-50 (hydrogen form) and AG-MP-1 (chloride form) were Soxhlet-extracted with methanol for 24 h. AG-MP-1 was then converted into its free-base form with 1 M NaOH and rinsed with Milli-Q water (Milli-Q SP. TOC, Nihon Millipore Ltd., Tokyo, Japan). Glass columns containing 6 ml (wet volume) of the cation resin and 12 ml (wet volume) of the anion resin were connected in series and conditioned by pumping about 1 l Milli-Q water through the resins. Blank samples were collected from each column after pumping 1–2 bed volumes of 0.01 M HCl solution just before and after application of the samples. A flow schematic of the DOM fractionation procedure is shown in Fig. 1. Details of the DOM fractionation

DOM 1
(AHS+HoN+HiA+BaS+HiN)

Step 1:
acidify to pH 2 and
pass through XAD8
column

→ DOM 2
(AHS)

XAD8 resin

Step 2:
elute 0.1 M NaOH

→ DOM 3
(HiF = HiA+BaS+HiN)

AG-MP-50
cation exchange
resin

Step 3:
pass through cation
and anion exchange
resins

→ DOM 4
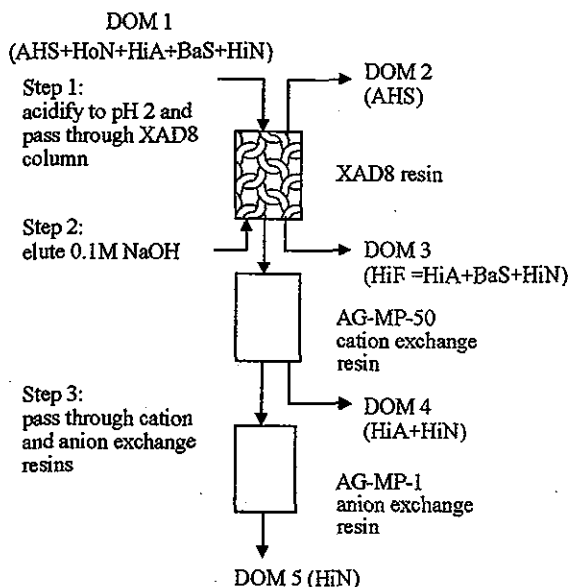(HiA+HiN)

AG-MP-1
anion exchange
resin

DOM 5 (HiN)

Fig. 1. Schematic diagram of the procedure for DOM fractionation. DOM fractions are AHS, HoN, HiA, BaS and HiN. The word hydrophilic fractions stands for HiF, which comprise HiA, BaS and HiN.

procedure can be found elsewhere [9]. DOM fractionation was done in duplicate for each sample. After fractionation, dissolved organic carbon (DOC) and ultraviolet absorbance (UV) were measured for DOM fractions 1–5 and for the blank samples. Each DOM fraction was calculated as follows:

$$\text{AHS} = \text{DOM2} \times (\text{elutant volume})/(\text{sample volume}) \quad (1)$$

$$\text{HoN} = \text{DOM1} - \text{AHS} - (\text{DOM3} - \text{B1}) \quad (2)$$

$$\text{BaS} = (\text{DOM3} - \text{B1}) - (\text{DOM4} - \text{B2}) \quad (3)$$

$$\text{HiA} = (\text{DOM4} - \text{B2}) - (\text{DOM5} - \text{B3}) \quad (4)$$

$$\text{HiN} = \text{DOM5} - \text{B3} \quad (5)$$

The blank DOC from the XAD-8 column during 0.1 M NaOH elution contained less than $0.7 \, \text{mg} \, \text{Cl}^{-1}$; its contribution to AHS would have been no more than $0.03 \, \text{mg} \, \text{Cl}^{-1}$. Thus, the blank DOC contribution to AHS was neglected. The blank UV contributions were neglected because the UV absorbance of the blank samples, B1, B2, and B3, was found to be $1–2 \times 10^{-3} \, \text{abs} \, \text{cm}^{-1}$, almost equal to that of Milli-Q water. The relative errors of the duplicated measurements for AHS, HoN, HiA, BaS, and HiN in the DOM fractionation (|measurement—average|/average) were 4.4%, 26.8%, 4.1%, 20.3%, and 22.1%, respectively.

After DOC and UV measurements, the remaining AHS samples were desalted by being passed through the

hydrogen-saturated cation exchange column, and then freeze-dried.

2.3. Trihalomethane formation potential determination

Sample filtrates, AHS and the HiF (HiF, equivalent to DOM3 in Fig. 1) were diluted with Milli-Q water to produce a DOC concentration of $1 \, \text{mg} \, \text{Cl}^{-1}$ before chlorination. Because each of the samples had the same DOC concentration, differences in reactivity with chlorine could be attributed to differences in the structural character of the samples. Freeze-dried AHS samples were reconstructed in Milli-Q water. The HiF samples, the pH of which remained at 2 after the DOM fractionation, were adjusted to about pH 7 with NaOH.

THMFP was measured according to the Standard Methods for the Examination of Drinking Water [12]. Samples were adjusted to pH 7 with phosphate buffer. Double-distilled sodium hypochlorite solution was added at a dose that produced a free chlorine concentration of $1–2 \, \text{mg} \, \text{l}^{-1}$ as Cl_2 after a reaction time of 24 h at 20°C. Reactions were performed in headspace-free containers (either 42 ml or 16 ml) and in the absence of light. Following the 24-h reaction period, free chlorine concentrations were determined by the o-trizine (OT) method. Excess chlorine was quenched with anhydrous sodium sulfite, and then concentrations of trihalomethanes were determined by the headspace method using gas-chromatography/mass-spectrometry (Hewlett Packard 6890/Hewlett Packard 5973, Yokogawa Analytical Systems Inc., Tokyo, Japan) equipped with a headspace autosampler (Hewlett Packard 7694). Analytical precision was typically less than ±2%.

2.4. Molecular size distribution analysis

High-pressure size exclusion chromatography (HPSEC) was performed at room temperature with a Hitachi L-6200 pump (Hitachi Ltd., Tokyo, Japan), a Hitachi L-4000 UV detector operating at 260 nm, a Hitachi D-2500 data integrator, and a Rheodyne rotary injection valve equipped with a 100-μl sample loop. A Waters Protein-Pak 125 modified silica column (Waters Co., Milford, USA) was used for this study. The column packing was selected for its low residual hydrophobicity and minimal ion-exchange capacity [13]. Mobile phases were composed of Milli-Q water buffered with phosphate to a pH of 6.8 and sodium chloride to yield an ionic strength of 0.1 M. The total exclusion elution time and the total permeation elution time were determined with blue dextran ($2 \times 10^3 \, \text{K}$) and acetone (58.4), respectively. Molecular weight standards were composed of sodium polystyrene sulfonates (35, 18, 8, 5.4, and 1.8 K) and acetone. The calibration curves were semi-log-linear over the range defined by our standards, showing an excellent correlation ($R^2 = 0.99$), and were

used to determine both number- and weight-averaged molecular weights. Sample filtrates were adjusted to an ionic strength of 0.1 M with the appropriate addition of 4 M NaCl, and to a pH of 6.8 with additions of phosphate buffer and HCl. AHS samples were prepared by dissolving the freeze-dried samples into the mobile phase solution. HiF samples were adjusted to an ionic strength of 0.1 M and a pH of 6.8 with additions of phosphate buffer, NaOH and NaCl. Typical precision for the determination of averaged molecular weights was ±3%.

2.5. Analytical methods

DOC measurements were conducted as non-purgeable DOC with a Shimadzu TOC-5000 total-organic-carbon analyzer equipped with a Pt catalyst on quartz wool (Shimadzu Co., Kyoto, Japan). At least 3 measurements were made for each sample, and analytical precision was typically less than ±2%. Potassium hydrogen phthalate was used as a standard.

UV absorbance was measured with a Shimadzu UV-2500 UV/VIS spectrometer at 260 nm using a quartz cell with a 1-cm path-length. All samples were adjusted to pH 2 with HCl before measurement. Milli-Q water was used for blank samples. UV absorbance at 260 nm was selected because (1) the maximum UV absorbance of phenolic, benzene carboxylic, and polycyclic aromatic compounds ($\pi - \pi^*$ transition), which are considered significant components of AHS, occurs at a wavelength of 200–290 nm [14,15]; (2) UV absorbance at 260 nm has been reported to be an index of the amount of humus-, lignin- and tannin-like compounds in water [16]; and (3) the presence of nitrate and borate does not affect the measurement of UV absorbance at 260 nm [15]).

3. Results

3.1. DOM-fraction distribution and UV absorbance to DOC ratio in lake water

DOM concentrations at the sampling point in Lake Kasumigaura ranged from 2.94 to 4.42 mg C l^{-1}, and averaged 3.46 mg C l^{-1} during the sampling period. The lake-water DOM at the sampling station exhibited a tendency to increase from spring to summer and then decline gradually. The maximum DOM concentration was observed in August.

Organic acids—AHS and HiA—dominated in Lake Kasumigaura, collectively accounting for more than 75% of the DOM as DOC (Table 1). In particular, the HiA fraction, which contains hydrophilic compounds such as sugar acids, fatty acids and hydroxyl acids, was found to be the most dominant fraction in all samples, constituting on average 46% of the DOM. AHS, comprising humic acids and fulvic acids, were the

Table 1
Dissolved organic matter (DOM) fraction distribution and ultraviolet absorbance to dissolved organic carbon (UV:DOC) ratio of water samples from Lake Kasumigaura

Fraction	DOM fraction distribution [%]	
	Average[a]	Range
AHS	32.3	26.0–39.8
HoN	7.9	0–19.0
HiA	45.6	39.4–61.3
BaS	8.6	3.7–13.8
HiN	5.6	0–10.9
	UV absorbance to DOC ratio [abs cm^{-1} l g C^{-1}]	
DOM	18.2	15.4–20.6
AHS	24.9	20.0–28.9
HiF	12.1	10.8–13.7

AHS: aquatic humic substances, HoN: hydrophobic neutrals, HiA: hydrophilic acids, BaS: bases, and HiN: hydrophilic neutrals. HiF: hydrophilic fractions = HiA + BaS + HiN.
[a] Number of samples = 12.

second most dominant fraction, accounting for 32%. The HiA and AHS fractions exhibited their peak concentrations in different months; HiA peaked in July, whereas AHS peaked in November. The HoN fraction, in which hydrocarbon, pesticides, carbonyl compounds, and synthetic detergents such as linear alkylbenzene sulfonate (LAS) were categorized, was found to vary considerably from 0% to 19%. Its peak values were observed in April and September. The BaS fraction, which contains proteins and amino acids, also varied from 4% to 14%. The HiN fraction—the carbohydrate-like DOM—was less than 10% in almost all samples. Easily biodegradable organic compounds such as proteins, amino acids, and carbohydrates may not be present in a great quantity in the lake water.

The UV absorbance to DOC (UV:DOC) ratio was significantly different among DOM, AHS, and HiF. All samples exhibited a common general relationship with respect to the UV:DOC ratio: AHS > DOM > HiF (24.9, 18.2, and 12.1 abs cm^{-1} l g C^{-1}) (Table 1). Seasonal variations in the UV:DOC ratios of DOM, AHS, and HiF were within ±15%, ±13%, and ±22% of the averages, respectively. The UV:DOC ratio of AHS was markedly greater than that of HiF; AHS contributed to a greater extent to the UV absorbance of DOM than did HiF (45% vs. 40%). In terms of DOC concentration, HiF were dominant over AHS, but in terms of UV absorbance, AHS were the most dominant DOM fraction in Lake Kasumigaura.

3.2. Molecular size distributions of DOM, AHS and HiF

All HPSEC chromatograms of DOM, AHS and HiF showed broad, monomodal size distributions with subtle

shoulders and small sub-peaks. Typical HPSEC chromatograms of DOM, AHS, and HiF are shown in Fig. 2. The weight-averaged to number-averaged molecular weight ratio (i.e., the analyte's polydispersity) was less than 2 in all cases, indicating that the DOM, AHS, and HiF molecules all occupy a relatively narrow size range and do not possess molecular weights that vary by orders of magnitude (Table 2). The weight-averaged molecular weights of DOM were relatively low, having an average of $780\,\mathrm{g\,mol^{-1}}$. AHS had a greater weight-averaged molecular weight than HiF, exhibiting an average value of $957\,\mathrm{g\,mol^{-1}}$, compared with $606\,\mathrm{g\,mol^{-1}}$ for HiF. AHS and HiF appeared to contribute mainly to the high- and low-molecular-weight fractions, respectively, of the DOM in Lake Kasumigaura. Seasonal variations in the weight-averaged molecular weights of DOM, AHS and HiF were not very pronounced. Molecular weights remained relatively constant, varying within $\pm13\%$, $\pm11\%$ and

$\pm24\%$ of the monthly average values of DOM, AHS and HiF, respectively. The variation in the molecular weight of HiF was reduced to $\pm16\%$ if the measurement in January was excluded; this measurement gave a considerably low-molecular-weight value for HiF.

It should be noted that UV absorbance detectors are somewhat selective, in that they will respond to or detect only those analytes that absorb at the wavelengths at which they are operating. DOM in Lake Kasumigaura is unlikely to contain a substantial amount of non-UV-absorbing DOM such as carbohydrates, as the low percentage fraction of HiN as indicated in Table 1. Nonetheless, there is a possibility that the HPSEC chromatograms obtained in this study are not completely consistent with "real" size distributions of DOM, AHS and HiF in Lake Kasumigaura. The determined molecular weights are probably less than their "real" values.
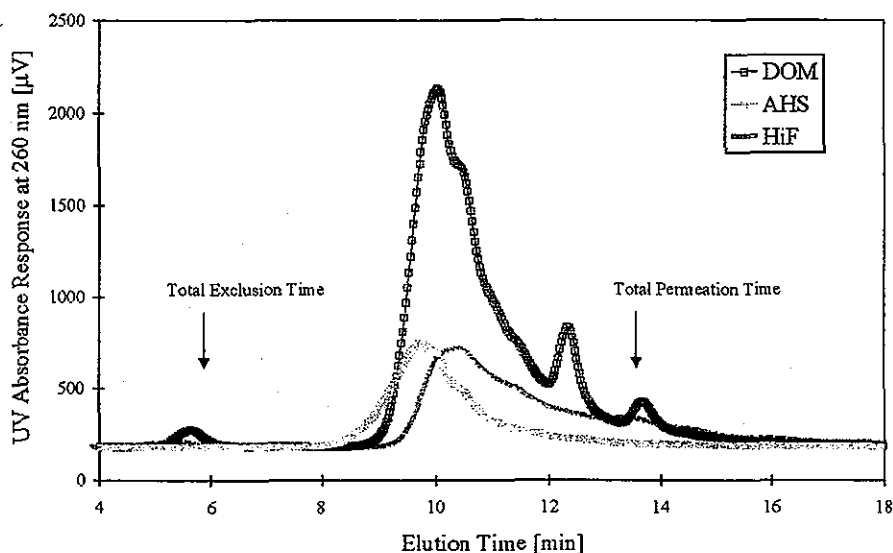

Fig. 2. Typical high-pressure size exclusion chromatograms of DOM, AHS and HiF in water from Lake Kasumigaura. The water sample was taken on September 10, 1997 at a point near the intake of a water treatment plant located on the shore of the lake.

Table 2
Molecular weight and polydispersity of dissolved organic matter (DOM), aquatic humic substances (AHS) and hydrophilic fractions (HiF) from waters of Lake Kasumigaura

Fraction	Weight-averaged molecular weight (M_w)	Number-averaged molecular weight (M_n)	Polydispersity (M_w/M_n)
DOM	780[a] (685–892)[b]	477 (402–539)	1.64 (1.53–1.78)
AHS	957 (862–1065)	512 (463–544)	1.87 (1.67–2.23)
HiF	606 (461–683)	381 (228–456)	1.61 (1.50–2.02)

[a] Average (number of samples = 12).

3.3. Specific trihalomethane formation potential of DOM, AHS and HiF

When normalized on a DOC basis, the specific THMFP (STHMFP) of AHS in Lake Kasumigaura was found to be slightly greater that of HiF. The average STHMFP of the AHS samples was $0.195 \mu mol$ $THM \, mg \, C^{-1}$, while the average HiF STHMFP was comparable at $0.176 \mu mol \, THM \, mg \, C^{-1}$ (Fig. 3). The paired t-test on the comparison of STHMFP between AHS and HiF showed a significant difference at $P < 0.05$ ($n = 12$); however, when we excluded one pair of data observed in July, which showed the largest difference, the t-test did not give a significant result. The DOM samples, ·
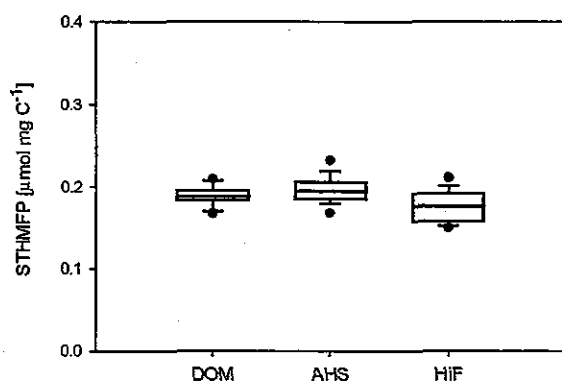

Fig. 3. Comparison of specific trihalomethane formation potential (STHMFP) between DOM, AHS and HiF in water samples from Lake Kasumigaura, 1997. The lower boundary of each box indicates the 25th percentile, a line within the box marks the mean, and the upper boundary of the box indicates the 75th percentile. Whiskers indicate the 90th and 10th percentiles, and solid dots indicate outlying points. Abbreviations are explained in the text.

as predicted from the observed STHMFP data on AHS and HiF, exhibited STHMFP values somewhere between those of HiF and AHS ($0.188 \mu mol \, THM \, mg \, C^{-1}$).

Seasonal variation in the DOM STHMFP was not great, although a noticeably low value was observed in March 1997 (Fig. 4). In contrast, the STHMFPs of AHS and HiF were relatively more variable during the year studied. AHS exhibited the lowest STHMFP in March, just as DOM did. The STHMFP then increased from spring to summer, peaking in August, and thereafter declined. The HiF STHMFP was the most variable but showed no clear seasonal trend; conspicuously low values were observed in April, July and December, and greater values in June and September.

No significant correlation was found for DOM, AHS or HIF between STHMFP and DOC concentration ($R^2 = 0.081$, 0.016 and 0.002; $P = 0.37$, 0.70 and 0.90, respectively). Thus, the variations in their STHMFP characteristics are independent of their concentrations.

4. Discussion

We evaluated DOM-fraction distribution, THMFP, UV:DOC ratio, and molecular size distribution in water samples from a eutrophic lake, Lake Kasumigaura. The samples were taken near the intake point of a water treatment plant located along the lakeshore. In the following discussion, we will focus mainly on the characteristics of DOM and its components from the viewpoint of THM precursors.

4.1. Trihalomethane formation potential

The reactivity of the non-humic fraction, namely HiF, was found to be comparable to that of AHS when
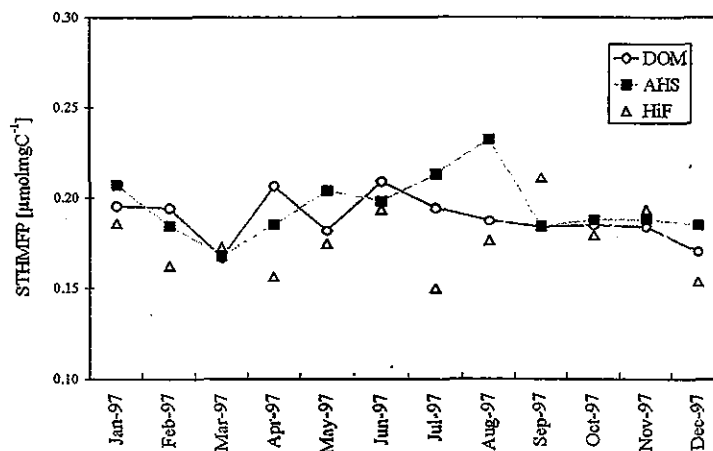

Fig. 4. Seasonal variations in specific trihalomethane formation potential (STHMFP) of DOM, AHS and HiF in Lake Kasumigaura.

THMFP was normalized on a DOC basis (STHMFP). This is the first time that the STHMFPs of AHS and HiF have ever been reported for DOM in a eutrophic lake. However, this finding appears to be somewhat contrary to the conventional belief that AHS behave as the principal THM precursor material. Nevertheless, this result is rather consistent with those reported recently in the literature. Owen et al. [6], in studying THMFP of different waters from reservoir, river and aquifer, showed that the non-humic fraction reacted with chlorine and produced THM per unit DOC at an extent comparable to the hydrophobic fraction (=AHS+HoN). Krasner et al. [17] also reported that fulvic and HiA in a reservoir showed comparable THMFP per unit DOC. Lin et al. [18] arrived at the similar result in a laboratory study using a commercial humic acid solution.

The comparable STHMFP between HiF and AHS may be attributed to the relative abundance of phenolic functional groups in HiF. Harrington et al. [19] reported in a study using pyrolysis gas chromatography/mass spectrometry and carbon-13 nuclear magnetic resonance that phenolic carbon content was the best indicator of reactivity between DOM and chlorine and gave a more quantitative indication of THM formation by DOM. The presence of phenolic-OH could lead to THM production owing to –OH, an electron-donating substituent. The –OH activates the ring that favors reaction with chlorine, resulting in the formation of THM and other disinfection by-products [20]. HiF have been known to contain a significant amount of phenolic structures [21]. In studying the characteristics of DOM in a leachate-polluted groundwater, Christensen et al. [22] found that the HiF contained about twice as many phenolic functional groups as fulvic acids. Galapate et al. [20] came to the same finding for treated industrial wastewaters. Thus, it is not unlikely that the STHMFP of HiF is comparable to that of AHS.

DOM composition, i.e., DOM-fraction distribution, appears to influence STHMFP markedly. When the DOM STHMFP is plotted against the percentage fractions of AHS or HiF, no significant correlation is found with either ($R^2 = 0.031$, $P = 0.59$ for AHS; $R^2 = 0.111$, $P = 0.29$ for HiF) (Fig. 5). Note that HiF comprise HiA, BaS and HiN. BaS include aromatic amines, protein, amino acids and aminosugars. It has been reported that hydrophobic BaS such as aromatic amines exist in a negligible quantity in lake and river waters [2,9]. With the exception of tyrosine and tryptophan, amino acids are insignificant THM precursors [23]. The HiN fraction is mainly carbohydrates, which have been reported to produce no THM under chlorination [24]. Both BaS and HiN are thus unlikely to be significant contributors to THM precursors. Therefore, it can be suggested that HiA are the major THM precursors in HiF. When the DOM STHMFP is plotted
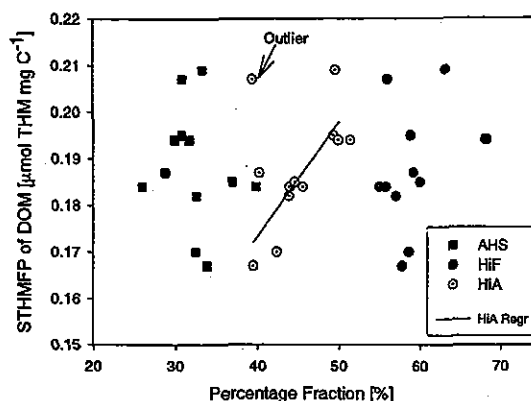

Fig. 5. Correlation between the specific trihalomethane formation potential (STHMFP) of DOM and the percentage fractions of AHS, HiF and HiA.

against the percentage fraction of HiA, excluding one result observed in April, a significant correlation is found between them ($R^2 = 0.63$, $P < 0.01$) (Fig. 5). This finding demonstrates that it is HiA, not AHS, that control the STHMFP of DOM in the water of Lake Kasumigaura, and also confirms that DOM composition is a crucial factor in regulating the characteristics of lake-water DOM as a THM precursor. One outlier comes from the water sample collected in April. For this sample, the DOM STHMFP was high, while the AHS and HiF STHMFPs were the lowest among all samples. Possibly, only in April, other DOM fractions, such as HoN, may have contributed substantially to the STHMFP of DOM.

It is interesting to note that the AHS STHMFP showed a considerable seasonal variation during the year studied. The AHS STHMFP increased approximately 40% from March to August. This indicates that significant seasonal changes in the characteristics of AHS in Lake Kasumigaura do occur: the composition of the AHS themselves may undergo an extensive change. Nevertheless, it remains to be seen whether the changes are caused by seasonal variations in either allochthonous or autochthonous AHS sources or by some physico-chemical or biological reactions or both inside the lake.

4.2. Molecular size distribution

The weight-averaged molecular weights of DOM, AHS and HiF in Lake Kasumigaura were found to be small, showing the average values of 780, 957 and 606 g mol^{-1}, respectively (Table 2). Thurman et al. [25] measured the molecular weight of AHS from various environments and concluded that an average molecular weight for humic substances from surface water was 1000–2000 g mol^{-1}. The molecular weights of AHS

determined in this study were around the lowest end of that range. Imai et al. [26] found that more than 85% of AHS in Lake Kasumigaura consisted of fulvic acids. The dominance of low-molecular-size fulvic acids in Lake Kasumigaura over high-molecular-size humic acids may be the reason for the relatively low molecular weight of the AHS. The molecular weight of HiF has not been reported before as far as we know; thus, the measured values cannot be compared with those in the literature. Nevertheless, it can be suggested that the molecular size of DOM belonging to HiF is very small.

Chin et al. [13] reported that for AHS samples from widely different origins the weight-averaged molecular weight had a linear relationship with their UV absorbance to DOC ratio. However, we did not find a linear relationship for AHS between the molecular weight and the UV:DOC ratio ($R^2 = 0.000$; $P = 0.97$). It appears that what Chin et al. [13] reported is only valid if the characteristics of AHS are by far different, namely if the absolute values of molecular size and UV absorptivity are quite different among samples. This also implies that the seasonal variation in the characteristics of AHS in Lake Kasumigaura is not great enough to result in a linear relationship between molecular weight and UV:DOC ratio. Analogously, for DOM and HiF, no linear relationship was found between molecular weight and UV:DOC ratio ($R^2 = 0.049$ and 0.134; $P = 0.49$ and 0.24, respectively). It is noteworthy, however, that a significant linear relationship is displayed between molecular weight and UV:DOC ratio when all data for DOM, AHS and HiF are plotted ($R^2 = 0.77$ and $P < 0.0001$) (Fig. 6). This result indicates a close positive interrelationship among molecular weight, UV absorptivity and hydrophobicity. The more hydrophobic the dissolved organic molecules, the greater the molecular weight and the higher the UV:DOC ratio.

The effects of molecular weight on STHMFP were not clearly seen; no significant correlation was observed between STHMFP and weight-averaged molecular weight for DOM, AHS and HiF ($R^2 = 0.125$, 0.174 and 0.018; $P = 0.26$, 0.17 and 0.69, respectively). When plotting all STHMFP data for DOM, AHS and HiF against weight-averaged molecular weight, a significant correlation is found ($R^2 = 0.162$; $P = 0.017$); however, the regression coefficient is very low, indicating that the difference in molecular weight is not a good explanation for the variation in STHMFP. The molecular weights of DOM, AHS and HiF are probably insensitive to their reactivity with chlorine in forming THMs.

4.3. UV absorbance to DOC ratio

The UV:DOC ratio appears not to be a good indicator for predicting the STHMFP of either DOM or AHS in Lake Kasumigaura. No positive significant correlation was found for DOM or AHS between STHMFP and the UV:DOC ratio ($R^2 = 0.17$ and 0.02; $P = 0.18$ and 0.69, respectively) (Fig. 7). However, for HiF, a significant correlation was observed between STHMFP and the UV:DOC ratio ($R^2 = 0.46$; $P < 0.05$). Since the major UV-absorbing component of DOM is AHS, the absence of a correlation for DOM between STHMFP and the UV:DOC ratio may be due to the small seasonal variation in the AHS characteristics in the year studied. The seasonal variation in the characteristics of HiF would have been relatively great, leading the variation in the UV:DOC ratio to reflect the difference in STHMFP. Since the major UV-absorbing components of HiF are HiA, this suggestion is consistent with what we found in our evaluation of the relationship between STHMFP and the percentage fraction of HiA.
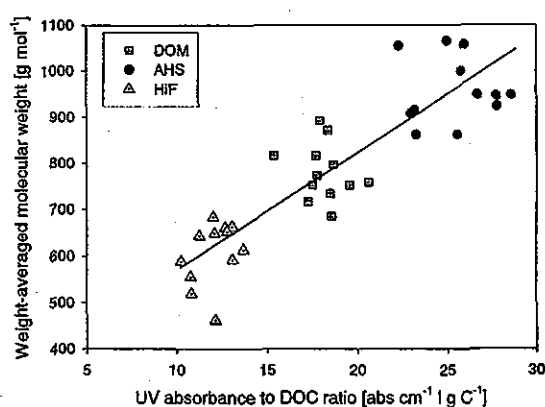

Fig. 6. Correlation for DOM, AHS and HiF between weight-averaged molecular weight and ultraviolet absorbance to dissolved organic carbon (UV:DOC) ratio.
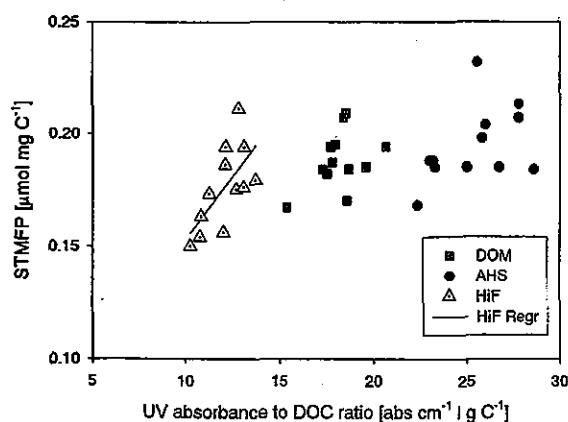

Fig. 7. Correlation for DOM, AHS and HiF between specific trihalomethane formation potential (STHMFP) and ultraviolet absorbance to dissolved organic carbon (UV:DOC) ratio.

Generally, the UV:DOC ratio is a good surrogate indicator of the change in DOM character and a predictor of the removal of disinfection by-products such as THM during water treatment. It is also used to evaluate the aromaticity of natural water [27]. However, for eutrophic lake waters such as those of Lake Kasumigaura, the UV:DOC ratio may be sensitive for only hydrophilic THM precursors, and may not be useful for representing AHS as THM precursors. Since AHS constitute the major portion of UV absorbance of DOM, the effectiveness of the UV:DOC ratio for representing DOM as a THM precursor becomes very ambiguous unless the DOM fractionation method is applied.

4.4. Implications for drinking water management

Drinking water quality standards for THMs have been promulgated on the basis of the concentrations of THM precursors in water. The importance of HiF over AHS as THM precursors becomes more pronounced when THM formation is evaluated in terms of concentration, that is, when THMFP is assessed in $\mu mol\, l^{-1}$ (Fig. 8). The THMFP of DOM was, on average, $0.650\, \mu mol\, THM\, l^{-1}$, exhibiting its maximum value of $0.827\, \mu mol\, THM\, l^{-1}$ in August. That maximum value is almost equal to the maximum allowable drinking water standard for THMs in Japan ($100\, \mu g\, l^{-1}$ for total THM, which is equivalent to $0.838\, \mu mol$ $THM\, l^{-1}$ when all THMs formed are assumed to be chloroform). The water of Lake Kasumigaura may not

be of suitable quality for drinking water supply. The THMFP of HiF is much greater than that of AHS: the average values for HiF and AHS are 0.374 and $0.229\, \mu mol\, THM\, l^{-1}$, respectively. This comparison reveals that HiF account for, on average, 57% of the THMFP of DOM, while AHS account for 35%. Therefore, we concluded that when waters from eutrophic lakes such as Lake Kasumigaura are used as sources of drinking water, lower-molecular-weight hydrophilic DOM, in particular HiA, should be of more concern as a THM precursor than AHS, from the viewpoint of water treatment practices.

Conventional water treatment processes such as coagulation–filtration usually remove larger molecular and more hydrophobic DOM [28]. After coagulation, the dominance of lower-molecular-weight materials increases. Activated carbon adsorption is applied in water treatment as an advanced process when dissolved organics must be removed. However, even with granular activated carbon (GAC), lower-molecular-weight and non-humic (hydrophilic) fractions of DOM are most difficult to remove [6,28]. GAC adsorption preferentially removes the humic fraction of DOM. Accordingly, it is probable that conventional water treatment processes—even those that use the GAC process—cannot effectively remove the dominant THM precursor in Lake Kasumigaura, low-molecular-weight HiA. New types of treatment process such as membrane filtration (nanofiltration) [28] may be needed when dealing with eutrophic lake waters as drinking water supplies.

Imai et al. [9] reported that in the waters of rivers flowing into Lake Kasumigaura AHS were dominant over HiA. This implies that most HiA in Lake Kasumigaura are likely to be autochthonous. Effective lake watershed management against eutrophication can lead to a substantial reduction of HiA levels in eutrophic lakes, and consequently can be quite effective for drinking water management as well.

5. Conclusions

DOM in water samples from Lake Kasumigaura was fractionated with resin adsorbents into 5 classes (AHS, HoN, HiA, BaS, and HiN) and its DOM-fraction distribution was evaluated. DOM, AHS, and HiF (= HiA + BaS + HiN) were also examined in terms of THMFP, UV:DOC ratio and molecular weight distribution.

AHS and HiA dominated in Lake Kasumigaura, collectively accounting for more than 75% of the DOM as DOC. In particular, the HiA fraction was found to be the most dominant fraction in all samples, constituting on average 46% of the DOM.

The THMFP of HiF, normalized on a DOC basis (STHMFP), was found to be comparable to that of
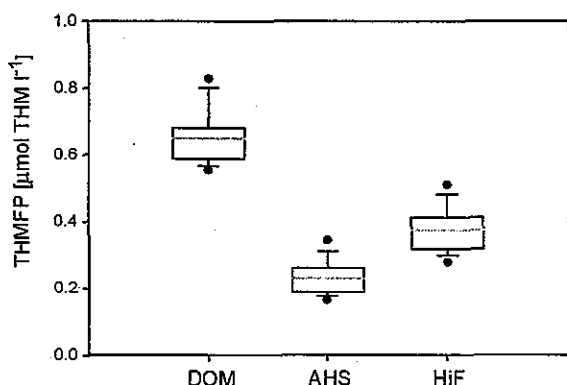

Fig. 8. Comparison of trihalomethane formation potential (THMFP) between DOM, AHS and HiF in water samples from Lake Kasumigaura, 1997. The lower boundary of each box indicates the 25th percentile, a line within the box marks the mean, and the upper boundary of the box indicates the 75th percentile. Whiskers indicate the 90th and 10th percentiles and solid dots indicate outlying points. Abbreviations are explained in the text. DOC concentrations of DOM, AHS, and HiF ranged 2.94–4.42, 0.88–1.40, and 1.89–2.74 mg C l^{-1}, respectively.

AHS (0.176 μmol THM mg C^{-1} vs. 0.195 μmol THM mg C^{-1}, respectively). The STHMFP of DOM was correlated significantly with the percentage fraction of HiA, but not with that of AHS or HiF, suggesting that it is HiA, not AHS, that control the characteristics of DOM as THM precursors in the waters of Lake Kasumigaura. This demonstrates that DOM composition influences substantially the characteristics of lake-water DOM as a THM precursor.

The importance of HiF, probably HiA, over AHS as THM precursors becomes more pronounced when THMFP is evaluated in terms of concentration (i.e., μmol THM l^{-1}). The THMFP of HiF was by far greater than that of AHS (mean 0.374 μmol l^{-1} vs. 0.229 μmol l^{-1}, respectively). HiF contributed to 57% of the DOM STHMFP, whereas AHS contributed 35%.

The UV:DOC ratio appears to be a sensitive surrogate parameter only for hydrophilic THM precursors, and it may be of much less use for predicting the quantities of DOM and AHS THM precursors. No significant correlation was found between the STHMFP and the UV:DOC ratio for either DOM or AHS, whereas a significant correlation existed between the STHMFP and UV:DOC ratio for HiF.

Molecular size distributions of lake-water DOM, AHS and HiF were determined by high-performance size exclusion chromatography and were found to exhibit a narrow size range and relatively low molecular weight. The weight-averaged molecular weights of DOM, AHS and HiF in the waters of Lake Kasumigaura were, on average, 780, 957 and 606 g mol^{-1}, respectively. It is noteworthy that the molecular size of dissolved organic molecules belonging to HiF, the major THM precursors in Lake Kasumigaura, was very small. No significant correlation was observed between the STHMFP and the weight-averaged molecular weight for DOM, AHS or HiF.

Acknowledgements

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