目的に、再度、実験を行った（以下、実験②とする）。実験②では、設定原水濁度を30度及び300度、凝集剤注入率を36mg/L 及び72mg/L の計 4 条件で、それぞれの条件における運転時間は実験①より長い48時間とした。実験②では、実験条件を変える前に、凝集混和槽、フロック形成槽、沈澱槽及び砂沪過塔を排水・洗浄することで、前条件の影響を排除した。実験②においては、両系統とも、実験①で使用した膜モジュールから新しい膜モジュールに交換して、実験を行った。

2.3　凝集剤

本研究で使用した従来型 PAC と高塩基度 PAC の成分を表-2に示す。Al_2O_3 濃度は、どちらの PAC も約10wt%であった。

PAC の塩基度（%）は、PAC の一般式を $[Al_2(OH)_nCl_{6-n}]$ としたとき、n/6×100 で表される。塩基度が異なると PAC に含まれるアルミニウム形態の存在比が変化し、塩基度が高いほど、モノマー状態のアルミニウム種（Al_a）の存在比が低く、ポリマー（Al_b）及びコロイド状態（Al_c）のアルミニウム種の存在比が多いことが報告されており[13),15~18)]、Al_a の含有量が高いほど残留したアルミニウム濃度が高い傾向が示されている[17),18)]。

表-2　本研究で使用した凝集剤の主な成分

系　統	凝集剤	塩基度 (wt%)	Al_2O_3 (wt%)	SO_4 (wt%)
従来型 PAC 系	従来型 PAC	51	10.1	2.8
高塩基度 PAC 系	高塩基度 PAC	72	10.5	2.8

2.4　分析・測定方法

濁度、pH、砂沪過圧力、膜差圧は、プラントに設置した連続計器にて測定した。

原水濁度及び沈澱水濁度は、原水調製槽及び沈澱水貯留槽にそれぞれ設置した表面乱反射式濁度計を用いて、30分毎に系統を切り替えて測定した。表面乱反射式濁度計は、濁度標準溶液（カオリン）を用いて校正した。砂沪過水濁度及び膜沪過水濁度は、レーザー式高感度濁度計（日本電色工業 NP500T）を用いて、30分毎に系統を切り替えて測定した。

pH は、pH センサーを用いて、原水調製槽及び凝集混和槽で測定した。

砂沪過圧力については、砂沪過一次圧力を砂沪過圧力とし、一次圧力を圧力センサーで測定した。膜差圧については、一次圧力と二次圧力の差とし、それぞれ圧力センサーで測定した。

連続計器による測定値は、データロガーで 5 分毎に記録した。

アルミニウム濃度、電気伝導率、総アルカリ度、沈澱水中フロックのゼータ電位及び粒径分布は、ポリエチレン瓶を用いて採水した試料を測定した。原水は原水調製槽、沈澱水は沈澱水集水枡から採水し、砂沪過水及び膜沪過水は配管途中のサンプリングコックから採水した。

アルミニウム濃度、マンガン濃度及び鉄濃度は、サンプルに濃度が 1 %となるように硝酸を添加後、測定した。試料を0.45 μm のメンブレンフィルター（ADVANTEC DISMIC 25AS45AN）で沪過して測定したものを溶解性アルムニウム濃度、溶解性マンガン濃度及び溶解性鉄濃度とし、沪過せずに測定したものを総アルミニウム濃度、総マンガン濃度及び総鉄濃度とした。アルミニウム濃度、マンガン濃度及び鉄濃度は、誘導結合プラズマ質量分析装置（ICP-MS Agilent 7500Ce）を用いて測定した。

電気伝導率は、電気伝導率計を用いて測定した。総アルカリ度は、自動滴定装置を用いて、pH4.8 までの硫酸消費量から算出した。

沈澱水中フロックのゼータ電位及び粒径分布は、沈澱水をポンプで後段の砂沪過及び膜沪過へ送水していることを考慮して、測定前に激しく攪拌した後に測定した。ゼータ電位は、ゼータ電位・粒度分布測定装置（ZEECOM ZC-3000）を用いて測定し、粒径分布はレーザー式高感度濁度計を用いて測定した。

3.　実験結果及び考察

3.1　実験原水水質

設定原水濁度毎の実験原水の主な水質測定結果（平均値）を表-3に示す。

原水濁度は、設定原水濁度 5 度の時は平均7.9度、設定原水濁度30度の時は平均36度、設定原水濁度300度のときは平均360度であり、設定原水濁度より高かった。系統間の差は 1 ～ 8 %程度だった。

表-3　原水水質測定結果

項目	単位	設定原水濁度		
		5度	30度	300度
pH	(−)	6.9	6.8	6.8
濁度	(度)	7.9	36	360
水温	(℃)	17.5	17.2	17.3
アルカリ度	(mg/L)	91.0	90.8	90.9
電気伝導率	(μS/cm)	379	379	379
総 Al	(mg/L)	0.035	0.20	1.1
溶解性 Al	(mg/L)	<0.001	<0.001	<0.001
総 Mn	(mg/L)	<0.001	<0.001	<0.001
溶解性 Mn	(mg/L)	<0.001	<0.001	<0.001
総 Fe	(mg/L)	0.003	0.007	0.004
溶解性 Fe	(mg/L)	<0.001	<0.001	<0.001

設定原水濁度が高くなると総アルミニウム濃度や総鉄濃度が上昇した。これは濁質成分のカオリンが原因と考えられた。一方で、アルカリ度及び電気伝導率については、設定原水濁度を変えても大きな変化はなかった。

3.2　濁度の除去性

(1)　凝集沈澱プロセスにおける濁度の除去性

図-2に、条件毎の沈澱水濁度の平均値及び凝集沈澱プロセスにおける濁度除去率を示す。

沈澱水濁度は、設定原水濁度5度～300度、凝集剤注入率36mg/L～72mg/Lの条件において、沈澱水濁度は約1度～約10度まで変化したが、同条件における高塩基度PAC系と従来型PAC系の沈澱水濁度にみられた差異は小さく、凝集沈澱プロセスにおける濁度除去率は同等となった。また、同一条件で再実験を行った場合においても、図-2に示した結果と同様に、高塩基度PAC系と従来型PAC系の沈澱水濁度に見られた差異は小さかった。

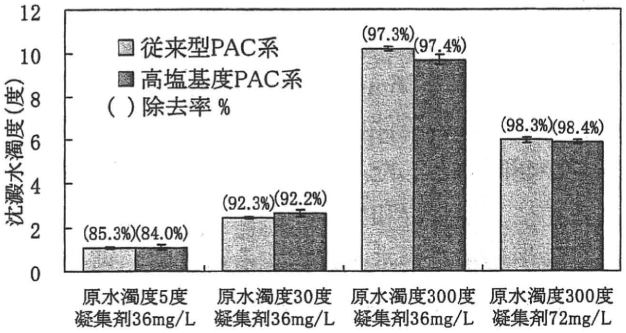


図-2　条件毎の沈澱水濁度平均値と凝集沈澱プロセスにおける濁度除去率（実験①）

(2)　膜沪過プロセス及び砂沪過プロセスにおける濁度の除去性

図-3に、実験①における膜沪過水及び砂沪過水濁度の経時変化を示す。砂沪過水濁度は、各々の系統で2塔分の結果を示した。

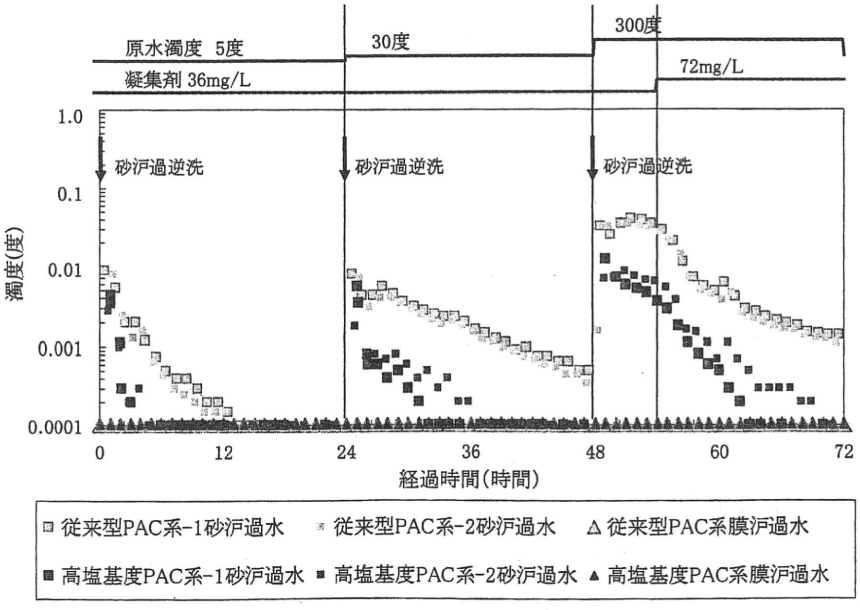


図-3　砂沪過水濁度の経時変化（実験①）

膜沪過水濁度については、両系統とも高感度濁度計の検出下限値（0.0001度）以下だった。

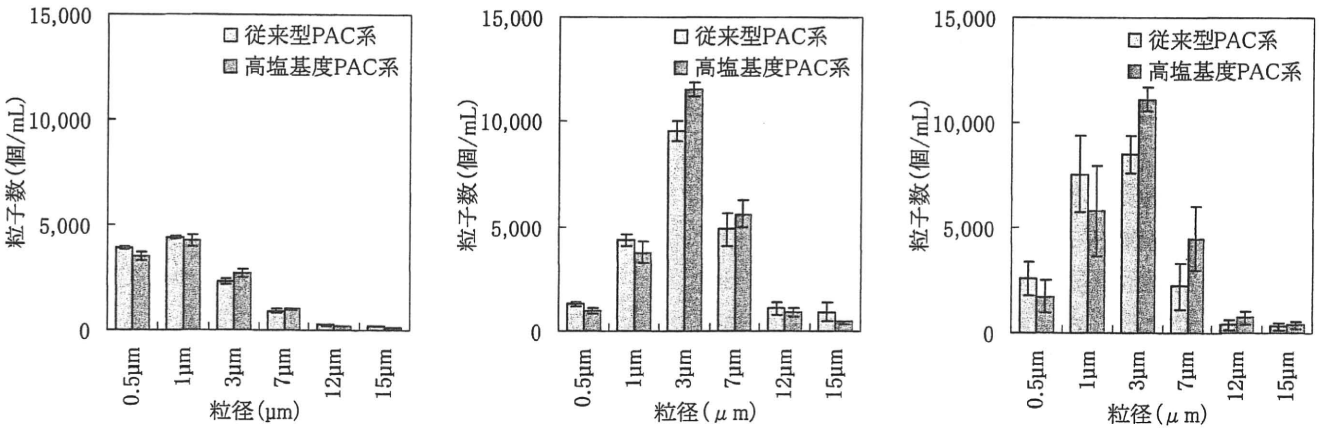
砂沪過逆洗直後の初期漏出濁度は、系統間に大きな差異は見られなかった。しかし、逆洗後、沪過時間が進むにつれて、高塩基度PAC系砂沪過水濁度が従来型PAC系砂沪過水濁度より低くなり、高塩基度PAC系砂沪過水は、従来型PAC系砂沪過水より洗浄後の初期漏出濁度の清澄化が早くなった。同じ系統内において、各々の砂沪過塔間で砂沪過水濁度に差異はほとんどなかったことから、砂沪過塔の違いによる性能の差は小さいと考えられた。また、実験②の4条件においても、同様の傾向が得られた。このことから、系統間で見られた砂沪過水濁度の差異は、各砂沪過塔の性能の違いではなく、砂沪過までの前処理の違いにより生じたものであることが示された。また、高塩基度PAC系で見られた初期漏出濁度の清澄化が早い傾向は、原水濁度条件や凝集剤注入率の変更によらず、両系統の沈澱水濁度が同程度であったにもかかわらず、全ての条件で見られた。このことから、凝集剤の性状の違いが濁度以外の因子に影響を与えたことによって、この傾向が生じているものと推測された。

海老江らによると、初期漏出期～清澄期の沪層では、径の大きなフロックから順に抑留が進行し、沪層上部ほど至適凝集領域に近いゼータ電位を持つフロックが優先的に除去され、ゼータ電位が低く、凝集力が弱いフロックほど沪層から流出しやすい[19]としている。このことを考慮すると、高塩基度PAC系のフロックは従来型PAC系のフロックより粒径が大きく、ゼータ電位は至適凝集領域に近いことが考えられた。このことを検証するために、実験②で、沈澱水中フロックの粒径分布及びゼータ電位の測定を行った。

図-4に、実験②の各運転条件における24時間運転後の沈澱水中フロックの粒径分布を示す。高塩基度PAC系のほうが従来型PAC系より大きい粒径の粒子が多い分布の傾向が見られ、Wuらのジャーテストによる結果[16]と同様の結果となった。前述したように高塩基度PACは、ポリマー（Al_b）及びコロイド状態（Al_c）のアルミニウム種の存在比が高いことから、架橋しやすいことがフロックの粒径が大きい一因と考えられた。沈澱水中フロックの粒径分布に差異がみられたのに対し、沈澱水中濁度は同程度であったことに対しては、何らかのフロックの性状違いに原因があるものと考えられる。

図-5に、実験②の各運転条件において、概ね8時間に1回採取した沈澱水中フロックのゼータ電位の測定結果を示す。ゼータ電位測定の結果、高塩基度PAC系のほうがゼータ電位の絶対値が小さくなり、至適凝集領域に近い傾向がみられた。両者のゼータ電位についてt-検定（有意水準 $\alpha = 0.05$）を行ったところ、凝集剤注入率36mg/Lの条件においては統計的に有意な差が見られた。

石川らは、コロイド滴定により、高塩基度



(a) 原水濁度 30度，凝集剤注入率 36mg/L　(b) 原水濁度 300度，凝集剤注入率 36mg/L　(c) 原水濁度 300度，凝集剤注入率 72mg/L

図-4　沈澱水に残留したフロックの粒径分布（実験②）

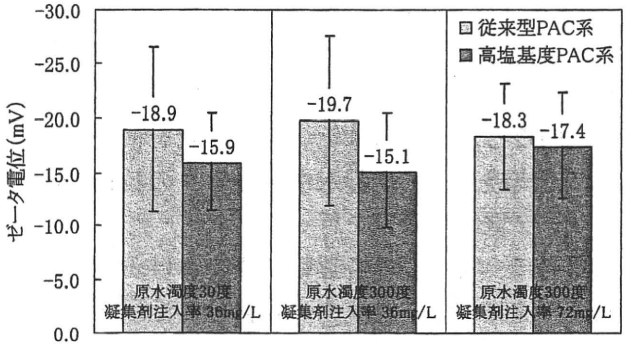


図-5　沈澱水に残留したフロックのゼータ電位（縦線は標準偏差）（実験②）

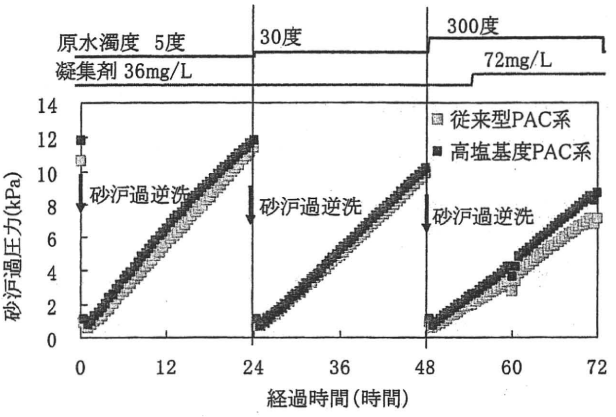


図-6　砂沪過圧力の経時変化（実験①）

PAC の荷電量が従来型 PAC より多いことを示している[21]。また、Yan らは、塩基度の異なる PAC を用いたジャーテストにより、pH 7 付近では塩基度が高いほどゼータ電位が高く[15]、至適凝集領域に近くなることを示している。本研究結果は、これら既往の研究と整合していた。

以上のことから、高塩基度 PAC 系で砂沪過初期漏出の清澄化が早く、フロックが捕捉されやすい原因は、高塩基度 PAC の荷電量が多いことやポリマー及びコロイド状態のアルミニウム種が多いことにより、粒径が大きくゼータ電位が至適凝集領域に近いフロックが形成されたためと考えられた。

近年のクリプトスポリジウム等対策による低濁度管理においては、砂沪過逆洗直後の初期漏出濁度をいかに抑制するかが重要となっており、初期漏出水を捨水するなどの対策が求められている[21]。高塩基度 PAC は初期漏出の清澄化が早いことから、高塩基度 PAC の使用により、捨水時間の短縮など、初期漏出濁度対策軽減化の可能性が示唆された。

(3)　砂沪過損失水頭の変化

図-6に、実験①における砂沪過圧力（一次圧力）の経時変化を示す。本実験装置は、砂沪過の二次圧が一定であるため、砂沪過圧力の経時変化は損失水頭の経時変化と同様と考えられる。

従来型 PAC 系と高塩基度 PAC 系で比較すると、設定原水濁度300度の条件（凝集剤注入率36mg/L 及び72mg/L）では、高塩基度 PAC 系で砂沪過圧力上昇が大きい傾向が見られたが、原水濁度 5 度及び30度の条件（ともに凝集剤注入率36mg/L）では、砂沪過圧力の上昇傾向に大きな差異は見られなかった。実験②の結果では、原水濁度300度の条件（凝集剤注入率36mg/L 及び72mg/L）でも、砂沪過圧力の上昇傾向に凝集剤の塩基度の違いによる差異は見られなかったため、高塩基度 PAC の使用による砂沪過損失水頭上昇への影響は限定的と考えられた。

一方で、原水濁度と凝集剤注入条件で比較すると、凝集剤中のアルミニウム濃度と原水濁度の比（AL/T 比）が最も大きい原水濁度 5 度、凝集剤 36mg/L の条件（AL/T 比：0.38）で最も砂沪過圧力の上昇が大きくなり、続いて原水濁度30度、凝集剤36mg/L の条件（AL/T 比：0.06）となり、条件によって差異がみられた。AL/T 比の小さい原水濁度300度の条件（凝集剤72mg/L の場合は AL/T 比：0.01）では、それぞれの運転期間が短いため一概に評価できないが、傾きから評価すると他の条件より砂沪過圧力の上昇は小さいものと考えられる。一般的に Al/T 比が大きいほど損失水頭は大きくなる[20] が、本実験でも Al/T 比が大きいほど砂沪過圧力上昇が大きくなる傾向を示した。

以上のことから、砂沪過圧力については、PAC の塩基度の違いより Al/T 比の違いほうが与える影響が大きかったため、高塩基度 PAC の使用は、従来型 PAC と比べても、砂沪過の操作性に大きな影響はないものと考えられた。

(4)　膜差圧の挙動

実験①における実験期間中の膜差圧挙動を図-7

に示す。膜差圧は、膜の一次圧と二次圧の差とし、25℃で補正した。

3時間に1回膜の物理洗浄を実施しているため、設定した3時間毎に膜差圧の回復が見られている。従来型PAC系と高塩基度PAC系を比較すると、示したデータは3日間という短期的な挙動では、凝集剤（塩基度）の違いによる明確な差異は見られなかった。

図-7をもとに、3時間に1回行っている物理洗浄の終了から次の物理洗浄の開始までの間に上昇した膜差圧をプロットしたものを図-8に示す。その結果、高塩基度PAC系膜差圧のほうが従来型PAC系膜差圧より、上昇幅が小さい傾向を示した。実験②では、膜モジュールを新しい膜モジュールに交換して行ったが、同じ傾向を示した。このことから、物理洗浄間で上昇した膜差圧で生じた差異は、膜モジュールの性能の違いによるものではなく、膜沪過までの前処理の違いにより生じたものと考えられた。

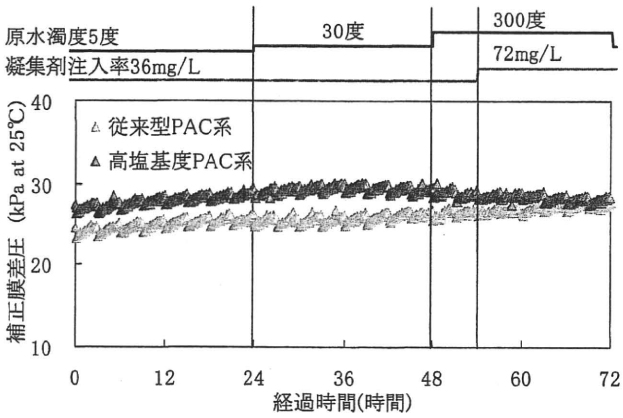


図-7　膜差圧の挙動（25℃補正）（実験①）

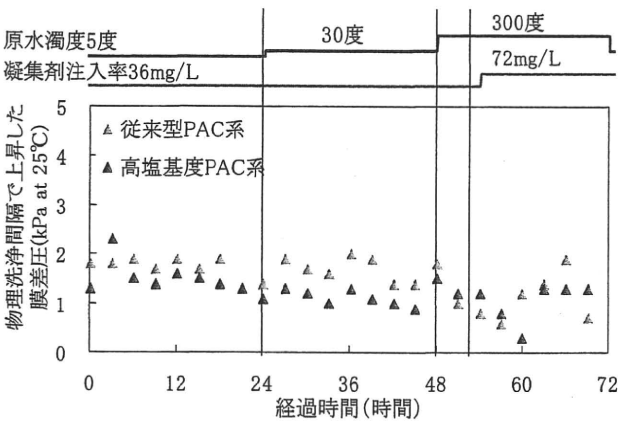


図-8　物理洗浄間隔で上昇した膜差圧（実験①）

凝集条件により、膜差圧の挙動や膜のファウリングが影響を受けることが知られており[23]、膜沪過原水のアルミニウム濃度[24]やフロックのゼータ電位[25]及び粒径分布[26]が影響する可能性があるとの報告もある。本研究では、膜沪過原水である沈澱水において、高塩基度PAC系と従来型PAC系でこれらの項目に差異が生じていることから、物理洗浄間で上昇した膜差圧で生じた差異の原因は、沈澱水中フロックにおける、ゼータ電位や粒径分布などの物性の違いや残留アルミニウム濃度が影響しているものと考えられた。詳細については今後の検討課題と考えられる。

加藤らは、34日間にわたる内圧式モノリス型セラミック膜を用いた実験で、高塩基度PACと従来型PACの膜沪過性を検討し、高塩基度PACは膜差圧上昇が抑制されることを示している[27]。酢酸セルロース膜を用いた本研究の結果や加藤らによる研究結果から考慮すると、高塩基度PACの使用による膜沪過性への負の影響はないものと推定されるが、今後は膜の材質や孔径の影響、長期的な膜沪過運転を行った場合のファウリングへの影響などについて、検討する必要があると考えられる。

3.3　アルミニウムの残留性

実験原水中の総アルミニウム濃度は原水濁度と共に上昇したが、溶解性アルミニウム濃度は0.001mg/L以下となり、定量下限値以下だった。

図-9に、実験①における従来型PACを使用した場合と高塩基度PACを使用した場合の沈澱水中総アルミニウム濃度と沈澱水中溶解性アルミニウム濃度の関係を示す。沈澱水中総アルミニウム濃度の分布は、両系統とも100μg/L～500μg/Lの範囲であった。高塩基度PAC系総アルミニウム濃度のほうが低くなる傾向もみられるが概ね同程度の分布を示し、沈澱水濁度と同様の傾向だった。その一方で、沈澱水中溶解性アルミニウム濃度の分布ついては、従来型PAC系沈澱水は30μg/L～70μg/Lの範囲だったのに対し、高塩基度PAC系沈澱水は10μg/L以下となり、高塩基度PAC系のほうが低くなった。

続いて、図-10に従来型PACを使用した場合と

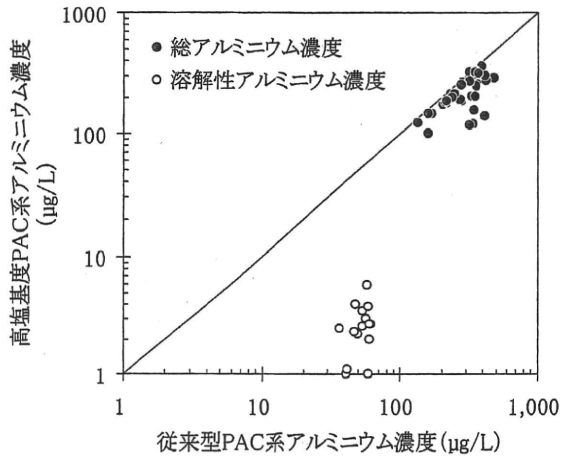


図-9　凝集剤による沈澱水中アルミニウム濃度の比較（実験①）

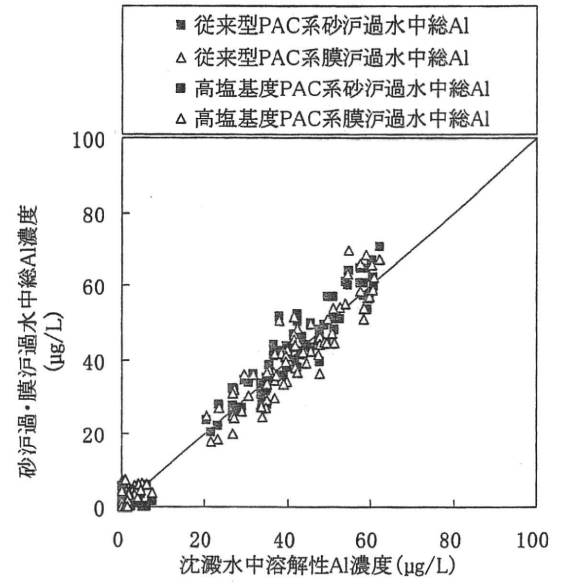


図-10　砂ろ過水中総アルミニウム濃度と膜沪過水中総アルミニウム濃度の関係（実験①）

高塩基度PACを使用した場合の沈澱水中溶解性アルミニウム濃度と砂沪過水及び膜沪過水中総アルミニウム濃度との関係を示す。砂沪過水及び膜沪過水中総アルミニウム濃度は20μg/L～70μg/Lの範囲で両者は同程度で、沈澱水中溶解性アルミニウム濃度と同程度だった。すなわち、砂沪過及び膜沪過により沈澱水中の懸濁態で存在するアルミニウムは除去できたが、溶解性のアルミニウムは除去できなかった。このことから、水道水中のアルミニウム濃度を低減するには、沈澱水中溶解性アルミニウム濃度を低減することが不可欠であることが示された。

以上のことから、高塩基度PACは従来型PACと同一の運転条件において、残留アルミニウムの低減効果があるものと考えられた。

4.　まとめ

地下水にカオリンを添加した実験原水について、パイロットスケールの実験装置にて、高塩基度PACの濁度の除去性とアルミニウムの残留性に関して検討した結果、以下の結論が得られた。

1)　高塩基度PACを使用した場合の凝集沈澱プロセスにおける濁度の除去性は、従来型PACを使用した場合と同等であった。

2)　高塩基度PAC系砂沪過水は、従来型PAC系砂沪過水より洗浄後の初期漏出濁度の清澄化が早くなった。

3)　高塩基度PAC系沈澱水中フロックは、従来型PAC系より粒径が大きく、ゼータ電位が至適凝集領域に近かった。これらによって、砂沪過水初期漏出濁度の清澄化が早まるものと考えられた。

4)　膜沪過水濁度は、高塩基度PAC系も従来型PAC系も、高感度濁度計の検出下限値以下だった。

5)　砂沪過損失水頭及び膜差圧に対する高塩基度PACと従来型PACの使用の差異は限定的だったことから、高塩基度PACを使用することに関する沪過性への影響は小さいと考えられた。

6)　高塩基度PAC系沈澱水中に残留する溶解性アルミニウムは、従来型PAC系より低かった。また、砂沪過水及び膜沪過水には沈澱水中溶解性アルミニウムと同程度残留した。そのため、水道水中アルミニウムの低減には、沈澱水中溶解性アルミニウムの低減が不可欠であることが示された。

7)　高塩基度PACは、従来型PACと同一の運転条件にて、水道水中アルミニウムを低減できることが示された。

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Practical Paper

Development of a model-based control system for membrane filtration process

Koji Kageyama, Takeshi Takemoto, Hideyuki Tadokoro and Masaki Itoh

ABSTRACT

Reduction of operational cost and certification of safety for treated water are required for the membrane filtration process for drinking water. Therefore a model-based control system is developed to reduce operational cost. A process model is used for the model-based control system that calculates the transmembrane pressure (TMP) in the future. This allows the model-based control system to optimize the coagulant dosage for the pretreatment process and the backwash interval for the membrane filtration process automatically. The cost reduction effect is verified using a pilot-scale plant.

Key words | coagulation, control, membrane filtration process, process model

Koji Kageyama (corresponding author)
Takeshi Takemoto
Energy and Environmental Systems Laboratory,
Hitachi Ltd, 7-2-1, Omika,
Hitachi, Ibaraki 319-1222,
Japan
Tel.: +81 294 52 9273
Fax: +81 294 52 9103
E-mail: *koji.kageyama.gf@hitachi.com*

Hideyuki Tadokoro
Information & Control Systems Division,
Hitachi Ltd, 5-2-1, Omika,
Hitachi, Ibaraki 319-1293,
Japan

Masaki Itoh
Department of Water Supply Engineering,
National Institute of Public Health,
2-3-6, Minami, Wako, Saitama 351-0197,
Japan

INTRODUCTION

The number of water purification plants using a membrane filtration process is increasing. At the end of 2007, there were 623 plants in Japanese municipalities which used the membrane filtration process. For purification plants larger than an intermediate class, surface water is sometimes used as raw water to be treated. In such cases, a pretreatment process is usually required in order to reduce membrane fouling. In the conventional membrane filtration process, the operational conditions of the pretreatment process and filtration process have been decided empirically. For example, the terms of the filtration process and backwash process are controlled by an electrical timer in the control board and the coagulation dosage is set as proportional to the turbidity of the raw water. These control techniques may be sufficient when the raw water is relatively clean (lacking large amounts of foreign substances), but they may be insufficient for plants that treat surface water with rather large fluctuations in water quality because of weather conditions such as rainfall. On the other hand, the requirement for the reduction of operational costs is increasing, and the conventional control technique has not always been able to do this.

If there is a simulation system by which the fluctuation of transmembrane pressure (TMP) can be predicted, the operational cost could be evaluated for various operational conditions. By using this simulation system, the most desirable operational conditions could be obtained. In order to predict the TMP, a process model is needed to explain the accumulation and detachment of foulants in the filtration process and backwash process.

It has been reported that the increase of TMP in the filtration process can be explained by a blocking model

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Table 1 | Assumed equations of process model

Model	Formula	Eq. no.
Standard blocking model	$\Delta P = \frac{\mu \times J \times C_0}{(1-(V_{ir}+V_r))^2}$	(1)
Accumulation of difficult to detach foulants	$\frac{dV_{ir}}{dt} = (C_1 \times \mathrm{Tu} + C_2 \times \mathrm{UV}_{260}) \times \exp(-C_3 \times \mathrm{PACl}) \times \exp(-C_4 \times \mathrm{temp}) \times (1.0 + C_5 \times \mathrm{cycle}) \times J$	(2)
Accumulation of easy to detach foulants	$\frac{dV_r}{dt} = (C_6 \times \mathrm{Tu} + C_7 \times \mathrm{UV}_{260}) \times \exp(-C_8 \times \mathrm{PACl}) \times J$	(3)
Removal of easy to detach foulants	$\frac{dV_r}{dt} = -C_9 \times V_r \times Q_b \times (1.0 + C_{10} \times \mathrm{temp}) \times (1.0 + C_{11} \times \mathrm{PACl}) \times (1.0 - C_{12} \times \mathrm{cycle})$	(4)

V_{ir}: index of difficult to detach foulants [-]; Tu: turbidity [NTU]; UV_{260}: ultraviolet absorbance [cm^{-1}]; PACl: PACl dose [$mg\,L^{-1}$]; temp: water temperature [°C]; J: filtration flux [$m\,s^{-1}$]; V_r: index of easy to detach foulants [-]; Q_b: flow rate for backwash [$m^3\,s^{-1}$]; Cycle: filtration process time [min]; ΔP: transmembrane pressure [Pa]; μ: viscosity of water [Pa s]; C_0: constant; $C_1 - C_{12}$: coefficients.

(Tambo 1994; Nishijima *et al.* 1998; Mingegishi *et al.* 2000; Kosvintsev *et al.* 2002; Susanto & Ulbricht 2008) or a cake filtration model (Fujita & Takizawa 1995; Bian *et al.* 2001; Lee *et al.* 2004; Yamamura *et al.* 2007). Both models include variables such as TMP and filtration flux, and the coefficients whose values differ depending on the raw water qualities. However, there are no reports in which the effect of each water quality item is shown as a mathematical expression. Also, there are no reports in which the effect of coagulant dosage on the reduction of membrane foulants is shown as a mathematical expression although there are some experimental results when the coagulation process is placed as the pretreatment for the membrane filtration process.

In this study, a process model is developed in which the accumulation and detachment amounts of membrane foulants can be calculated by the concentration of each raw water quality item and operational conditions. When the calculation procedure is established by which the operational cost can be calculated from the calculated TMP given by the process model, the operational cost can be obtained in advance from raw water qualities and operational conditions. In this study, coagulant dosage and backwash interval are selected as the items to be optimized.

MATERIAL AND METHODS

Process model for prediction of TMP

As a prerequisite for use in an automated control system, the main requirements for the process model are as follows.

- All input items should be measured automatically
- The number of coefficients (adjustable parameters) should be as small as possible
- Variation of TMP with time in the future should be calculable
- Both the filtration process and the backwash process should be provided in the model

To satisfy these requirements, equations shown in Table 1 were assumed. The foulants were classified into 'difficult to detach foulants' and 'easy to detach foulants'. Both difficult and easy to detach foulants were expressed by a standard blocking model. The indices of foulants in each of the equations were modelled as functions composed of raw water quality items. These functions express the relationship between increase and decrease of a property

Table 2 | Calibrated values of coefficients

C_1	3.3×10^{-8}
C_2	5.8×10^{-7}
C_3	3.2×10^{-2}
C_4	5.4×10^{-1}
C_5	1.3×10^{-6}
C_6	1.7×10^{-10}
C_7	2.1×10^{-6}
C_8	5.7×10^{-15}
C_9	8.0×10^{-1}
C_{10}	2.8×10^{-2}
C_{11}	7.4×10^{-2}
C_{12}	4.1×10^{-3}

simply based on experiments carried out previously. The values of the coefficients in these equations were calibrated by actual measurements of a pilot-scale facility. The calibrated coefficients are shown in Table 2. The calculated values of TMP showed good agreement with measurements and the mean error was 5.1–6.7 kPa.

Procedure for calculating operational cost

The formulae for computation of each evaluation index are shown in Table 3. The formulae for computation of each physical value are shown in Table 4. The TMP predicted by the process model shown above was used for the calculation of power consumption of pumps and the calculation of the interval of chemical cleaning. The chemical cleaning cost was calculated as one chemical cleaning unit cost that resulted when the TMP exceeded a set value. The membrane module replacement cost was calculated as one membrane replacement unit cost that resulted when pure water flux, which decreased at each chemical cleaning process, fell below a set value. Sometimes the membrane module is replaced regularly regardless of decline of its performance. Therefore the case in which the membrane module replacement cost was involved in the evaluation index and the case in which it was not involved were considered.

Table 3 | Equations for computing evaluation indices

	Eq. no.
Evaluation indices	
Operational cost [¥ m^{-3}] = power cost [¥ m^{-3}] + chemical cost [¥ m^{-3}] + sludge disposal cost [¥ m^{-3}] + chemical cleaning cost [¥ m^{-3}] + membrane replacement cost [¥ m^{-3}]	(5)
Power cost	
Power cost [¥ m^{-3}] = (power cost by filtration pump [¥] + power cost by backwash pump [¥] + power cost by dewatering equipment [¥])/effective quantity of water [m^3]	(6)
Power cost by filtration pump [¥] = unit price of power [¥ kWh^{-1}] × power consumption by filtration pump [kWh]	(7)
Power cost by backwash pump [¥] = unit price of power [¥ kWh^{-1}] × power consumption by backwash pump [kWh]	(8)
Power cost by dewatering equipment [¥] = unit price of power [¥ ton^{-1}] × (sludge quantity from suspended solids [ton] + sludge quantity from organic substances [ton] + sludge quantity from coagulant [ton]) × exp(−0.03 × standard value of coagulant dosage [mg L^{-1}])/exp(−0.03 × coagulant dosage [mg L^{-1}])	(9)
Chemical cost	
Chemical cost [¥ m^{-3}] = (cost for coagulant consumption [¥] + cost for NaClO consumption [¥])/effective quantity of water [m^3]	(10)
Cost for coagulant consumption [¥] = unit price of coagulant [¥ kg^{-1}] × dosage of coagulant [mg L^{-1}] × total quantity of filtrated water [m^3] × 10^{-3}	(11)
Cost for NaClO consumption [¥] = unit price of NaClO [¥ kg^{-1}] × dosage of NaClO [mg L^{-1}] × total quantity of backwash water [m^3] × 10^{-3}	(12)
Sludge disposal cost	
Sludge disposal cost [¥ m^{-3}] = (sludge quantity from suspended solids [ton] + sludge quantity from organic substances [ton] + sludge quantity from coagulant [ton]) × unit price for sludge disposal [¥ ton^{-1}]/effective quantity of water [m^3]	(13)
Chemical cleaning cost	
Chemical cleaning cost [¥ m^{-3}] = unit price for chemical cleaning [¥ $times^{-1}$ Qty.$^{-1}$] × times for chemical cleaning [times] × number of membrane modules [Qty.]/effective quantity of water [m^3]	(14)
Times for chemical cleaning [times] = calculation period [d]/predicted interval of chemical cleaning [d $times^{-1}$]	(15)
Membrane replacement cost	
Membrane replacement cost [¥ m^{-3}] = unit price of membrane replacement [¥ $times^{-1}$ Qty.$^{-1}$] × times for membrane replacement [times] × number of membrane modules [Qty.]/effective quantity of water [m^3]	(16)
Interval of membrane replacement [d $times^{-1}$] = interval of chemical cleaning [d $times^{-1}$] × log (decreasing rate of filtration performance [%]/100)/log (recovery rate by chemical cleaning [%]/100)	(17)

Table 4 | Equations for computing physical values

	Eq. no.
Effective quantity of water [m^3] = total quantity of filtrated water [m^3] − total quantity of backwash water [m^3]	(18)
Power consumption by filtration pump [kWh] = (0.163 × (filtration flux [$m\,d^{-1}$] membrane area [m^2]/24/60) × (mean TMP [kPa] + water head at the outlet [kPa] + pipe resistance [kPa])/9.81)/pump efficiency [-]) × (filtration process time[s]/3,600)	(19)
Power consumption by backwash pump [kWh] = (0.163 × flow rate for backwashing [$m^3\,min^{-1}$] × (mean TMP [kPa]/9.81) × (backwash flux [$m\,d^{-1}$]/filtration flux [$m\,d^{-1}$])/pump efficiency [-]) × (backwash times [s]/3,600)	(20)
Power consumption by dewatering equipment [kWh] = power cost by dewatering equipment [¥]/unit price of power [$¥\,kWh^{-1}$]	(21)
Sludge quantity from suspended solids [ton] = total quantity of filtrated water [m^3] × suspended solids in raw water [$mg\,L^{-1}$] × 10^{-6}	(22)
Sludge quantity from organic substances [ton] = total quantity of filtrated water [m^3] × (100/58) × TOC in raw water [$mg\,L^{-1}$] × 0.7(1.0 − exp(−0.35 × dosage of coagulant [$mg\,L^{-1}$ as AL])) × 10^{-6}	(23)
Sludge quantity from coagulant [ton] = total quantity of filtrated water [m^3] × dosage of coagulant [$mg\,L^{-1}$] × 10^{-6}	(24)
Mean TMP [kPa] = (TMP just after backwash [kPa] + TMP just before backwash [kPa])/2.0	(25)
Pipe resistance [kPa] = flow coefficient [-] × (10.666 × (number of membrane modules [Qty.] × membrane area [m^2] × filtration flux [$m\,d^{-1}$]/24/3,600)$^{1.85}$) × length of pipe [m]/(100$^{1.85}$ × pipe diameter [m]$^{4.87}$)	(26)

Effect of model-based control system

The process model and the calculation procedure for operational cost were implemented in control software with an optimization algorithm, and the verification experiments were carried out using the facility illustrated in Figure 1. The raw water was surface water from the Kuji River in Ibaraki Prefecture, Japan. It was first treated in the Mn removal column, then polyaluminium chloride (PACl) was added with rapid mixing. After that, it was filtered by the membrane. For the control evaluation, two systems were used which could treat the water at the same quality level. The external pressure type hollow fibre membrane modules were used. The membrane material was polyvinylidene difluoride (PVDF). The filtration area was 23 m^2 per module, and the nominal pore size was 0.1 μm. The turbidity was measured with a turbidity meter TR-502 (Kasahara Chemical Instruments). The kaolin turbidity standard was used so the unit for turbidity in this study was $mg\,l^{-1}$. The index of organic substances, UV_{260}, was measured by an ultraviolet absorptiometer DIAMON with a 1 cm quartz cell after removal of suspended solids by filtration through a paper filter of 1 μm pore size.

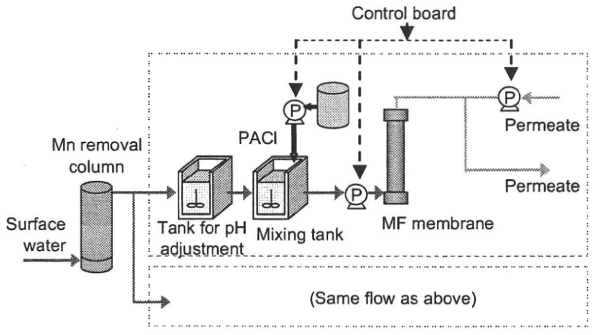

Figure 1 | Process flow of experimental facility.

One system was controlled by the model-based control method while the other was controlled by the conventional control method. This conventional control method was composed of coagulants dosage control, in which the dosage was proportional to turbidity of the raw water, and filtration cycle control, in which the filtration process time was set to a constant value (30 or 45 min).

Operational conditions

In each system, the generated water amount (filtered water amount minus water amount for backwash) was set to 2.5 $m^3\,h^{-1}$ and 1.25 $m^3\,h^{-1}$ and the recovery rate was set to 95%. The lower limit of filtration time was set to 20 min while the upper limit was set to 120 min. The lower limit of PACl dosage was set to 5 $mg\,l^{-1}$ and the upper limit

Table 5 | Conditions for each run

Run No.	Generated water amount	Evaluation indices (in Table 3)	Upper limit of PACl dosage
Run-1		①②③④⑤	None
Run-2	$2.5\,m^3\,h^{-1}$		Half of the actual plant (rapid filtration process)
Run-3		①②③④	
Run-4	$1.25\,m^3\,h^{-1}$		None

to $60\,mg\,l^{-1}$. To evaluate the effect of restriction of PACl consumption, another case was also considered in which the upper limit of PACl was set to half that of an actual purification plant which treats water by a rapid sand filtration method.

In the verification, four kinds of experiment shown in Table 5 were carried out. When the TMP of either or both of the model-based control and the conventional control exceeded 150 kPa, operation of the experimental facility was suspended and chemical cleaning was carried out. Then, the next run was started. The operational cost was estimated from the data obtained until the chemical cleaning was done. The effect of model-based control was evaluated by comparing the results of the operational cost for the two controls.

RESULTS AND DISCUSSION

The transitions of raw water qualities are shown in Figure 2. The lowest value of the turbidity of the raw water was $2\,mg\,l^{-1}$, while the highest value was over $100\,mg\,l^{-1}$. The mean value of the turbidity of the raw water was $14.4\,mg\,l^{-1}$. The concentration of dissolved Mn was below $0.007\,mg\,l^{-1}$, and the UV_{260} was below $0.30\,cm^{-1}$.

The transitions of operational conditions and TMP are shown in Figure 3. In Run-1, the PACl dosage of

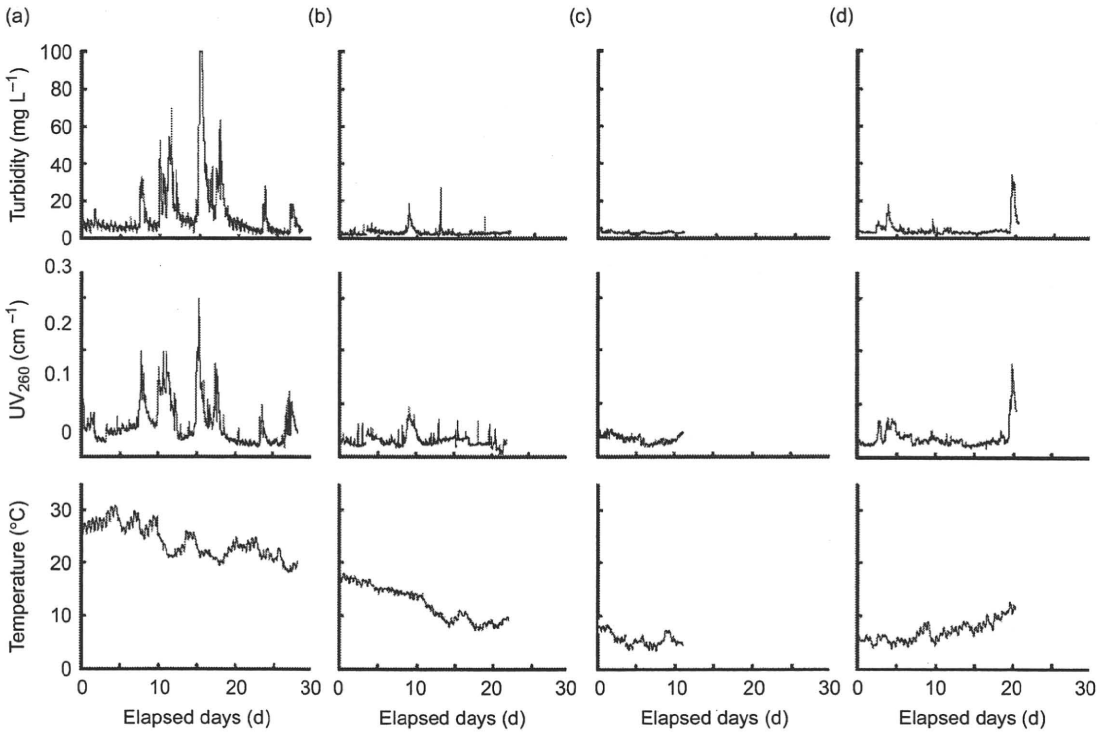

Figure 2 | Transitions of raw water qualities: (a) Run-1; (b) Run-2; (c) Run-3; (d) Run-4.

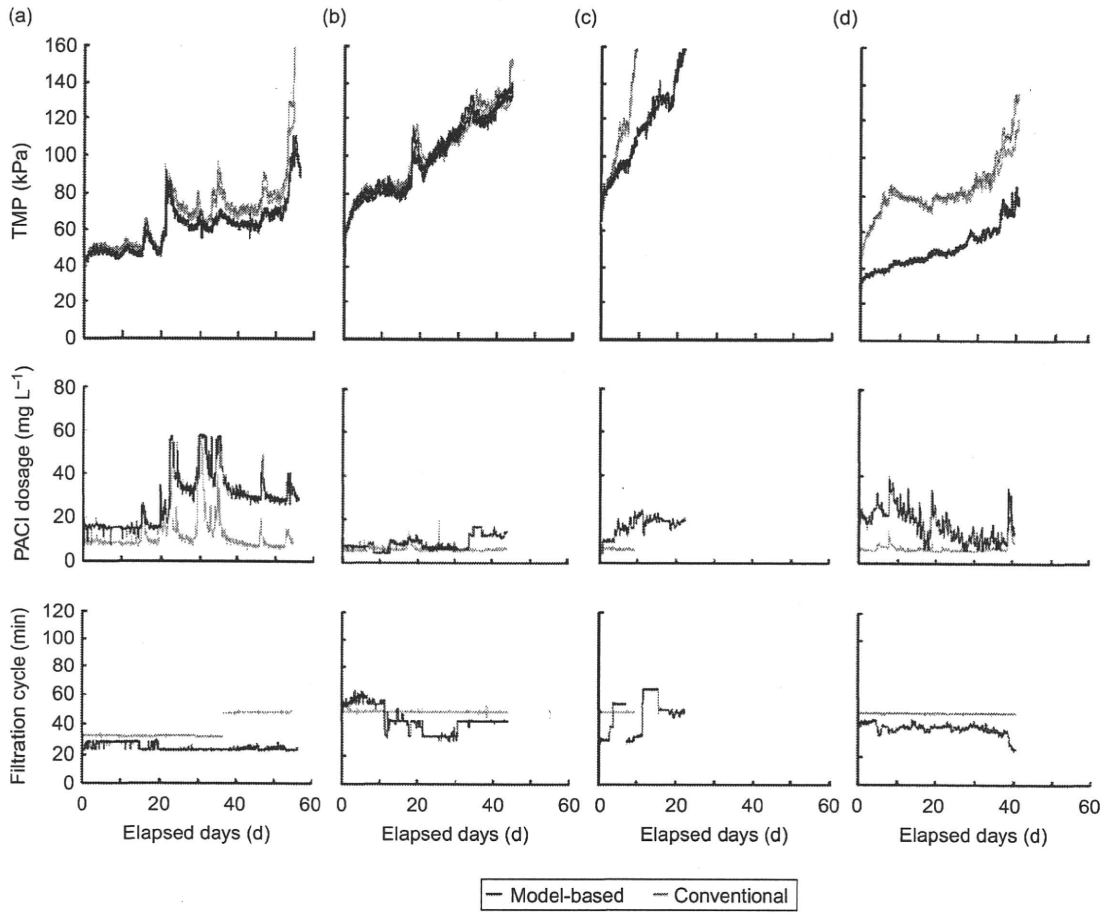

Figure 3 | Transitions of TMP and operational conditions: (a) Run-1; (b) Run-2; (c) Run-3; (d) Run-4.

model-based control fluctuated between two and three times higher than that of conventional control. The filtration process time of model-based control was about 25 min, which was shorter than that of conventional control. For the conventional control, the filtration process time was changed from 30 min to 45 min on the 37th day. In Run-1, TMP of the model-based control and the conventional control were almost the same for the first 23 days, but from 24 days the deviation increased. On the 55th day, the TMP of the conventional control was over 150 kPa, and the operation was changed to the chemical cleaning mode.

In Run-2, the PACl dosage of model-based control was lower than that of Run-1, because the upper limit of PACl dosage was set. On the 44th day, the TMP of the conventional control was over 150 kPa, and the operation was changed to the chemical cleaning mode.

In Run-3 and Run-4, the upper limit of PACl dosage was released. As a result, the PACl dosage of model-based control was about 2–3 times higher than that of the conventional control. The rate of increase of TMP was much higher than in Run-2, and between the 8th and 9th days, the TMP exceeded 150 kPa. Run-3 was continued until the TMP of the model-based control also exceeded 150 kPa. Finally, on the 20th day, the operation was changed to the chemical cleaning mode.

In Run-4, the filtration flux was decreased. The same as in Run-3, the PACl dosage of model-based control was higher and the filtration process time was shorter than the conventional control. Although the TMP of

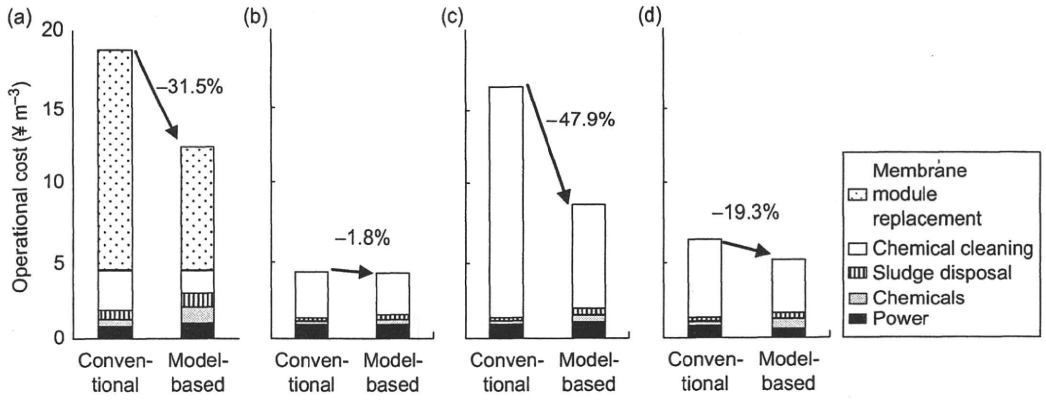

Figure 4 | Operational cost comparison: (a) Run-1; (b) Run-2; (c) Run-3; (d) Run-4.

the model-based control and the conventional control did not exceed 150 kPa, the operation was suspended because of the time limit of the experiment.

Based on the results shown in Figure 3, operational cost was estimated for each run. The interval of chemical cleaning of the model-based control was calculated by extrapolation of the TMPs shown in Figure 3 excluding Run-3. Figure 4 shows the operational cost results of each run.

In Run-1, the effect of cost reduction was 31.5%. The chemical cost and sludge disposal cost were higher in the model-based control, because the coagulant dosage of the model-based control was higher than the conventional one. The power cost was also higher because the sludge dewatering ability had fallen because of high coagulant dosage. However, the increase of TMP was restricted because substances such as dissolved organic matter, which may be the dominant difficult-to-detach foulants, were thought to be absorbed in large flocs generated by the high dosage coagulant. As a result, because the proportion of membrane module replacement cost and chemical cleaning cost was larger, the operational cost was reduced overall.

In Run-2, owing to the difference of the upper limit and the evaluation indices, the PACl dosage was almost the same. That is why the cost reduction effect was only 1.8%.

In contrast, the operational cost was cut almost in half in Run-3. The membrane module replacement cost was not included in evaluation indices in Run-3, and the effect of cost reduction was thought to be less than that of Run-1 at first. However, the accumulation rate of foulants on the membrane was faster because the water temperature was low, reaching a minimum of 5°C. As a result, TMP grew rapidly and chemical cleaning cost increased. Then, a larger effect on operational cost reduction was obtained than in Run-1. When the water temperature was low, the TMP increased because the viscosity of water increased. And the coagulation reaction of PACl was slow when the water temperature was low. It followed from this that the effect of pretreatment was reduced. In addition to these findings, the detachment effect of foulants on the membrane decreased when the water temperature was low. For these reasons, the TMPs in Run-3 were thought to increase rapidly.

In Run-4, the filtration flux was decreased. Therefore the effect of operational cost reduction was less than in Run-3 and the model-based control had a 19.3% operational cost reduction.

As shown above, although there were differences in the degree of the effect between 1.8% and 47.9%, the operational cost reduction by model-based control was verified for all runs. The extent of the reduction of operational cost and the optimum control conditions were found to differ due because of conditions of the upper limit of PACl dosage, filtration flux and evaluation indices.

The operational conditions obtained in this study cannot be used, for example, when the filtration flux, water resource or the membrane material is different. However, the model-based control method has a high

flexibility because it consists mainly of the mathematical model and the procedure for calculating operational cost. Therefore it is possible to obtain the optimum operational conditions and control the facility just by changing the values in the software and carrying out the calibration. If the fouling phenomena do not differ much, this control method can be adapted to other membrane modules even though the manufacturer or the material is different.

CONCLUSIONS

In this study, a model-based control system was developed in which the coagulant dosage for the pretreatment process and the backwash interval for the membrane filtration process were automatically optimized based on the process model by which the future TMP could be calculated. From the results of a pilot-scale experiment, the operational cost was thought to be reduced by as little as 1.8 to as much as 47.9%. The extent of the reduction of operational cost and the optimum control conditions were found to differ depending on the conditions of the upper limit of PACl dosage, filtration flux and evaluation indices.

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Determination of EDTA in Water Samples by SPE-Gas Chromatography/Mass Spectrometry

Reiji KUBOTA*, Maiko TAHARA*, Kumiko SHIMIZU*, Naoki SUGIMOTO*, Tetsuji NISHIMURA*

**Division of Environmental Chemistry, National Institute of Health Sciences, Kamiyoga 1-18-1, Setagaya-ku, Tokyo 158-8501, Japan*

ABSTRACT

Japan's recommended method of EDTA determination is complex and time-consuming. In this study, a new method to prepare the solution to determine EDTA in water by solid-phase extraction-GC/MS was developed. Recovery yields were excellent with values ranging from 98.1 to 100.5%. Due to this method's ease and simplicity, it is suggested that this approach be adopted as Japan's recommended method for EDTA analysis. The method was applied to assess the concentrations of EDTA in river water from three regions of Japan. Median concentration of EDTA in river water samples was 115 μg/L, and the concentrations ranged from 18.8 to 443 μg/L. The highest concentration of EDTA (443 μg/L) was observed in Tsurumi River. Sewage treatment plant (STP) effluent significantly contributed to high EDTA levels.

Keywords: EDTA, GC/MS, river water, solid-phase extraction.

INTRODUCTION

Ethylenediaminetetraacetic acid (EDTA) is one of the most widely employed aminopolycarboxylic acids with uses in the pharmaceutical, food, personal care product, and agricultural industries. Because of its widespread use, high water solubility, and low biodegradability in the environment, EDTA has emerged as a persistent organic pollutant in the aquatic environment. EDTA has been detected at μg/L level in various anthropogenically influenced waters (including surface water and sewage water) in many studies worldwide (Kari and Giger, 1995; Knepper *et al.*, 2005). Thus, control of EDTA in drinking water is critical.

In Japan's drinking water quality control, standards are categorized into three groups. The first group is composed of legally binding standards (Drinking Water Quality Standards; 50 items). The second group consists of non-legally binding standards (Complementary parameters to set the target quality management; 27 items (128 compounds)). The third group contains 44 items which require further studies for risk assessment; EDTA is presently categorized into the third group and the standard value is 0.5mg/L. The standard analytical methods for these items are legally bound and the Japanese Standard Methods for the Examination of Water are established for the analysis of second and third group items, including EDTA analysis. In these standard methods, EDTA concentration is determined by the evaporation of water, methyl ester derivatization, dichloromethane extraction, and then gas chromatography/mass spectrometry. However, sample preparation is complex and time-consuming, because this method includes evaporation of water sample from 100 mL to ca. 2 mL using rotary evaporator and derivatization processes (1 h heat treatment), and these processes take a long time. In this study, we investigated how to improve the analytical procedure. Various analytical methods have been reported using high performance liquid

Address correspondence to Reiji Kubota, Division of Environmental Chemistry, National Institute of Health Sciences, Email: reijik@nihs.go.jp
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chromatography (Nowack *et al.*, 1996; Kemmei *et al.*, 2009), ion chromatography/mass spectrometry (Bauer *et al.*, 1999; Knepper *et al.*, 2005), gas chromatography/mass spetrometry (Nishikawa and Okumura, 1995), and liquid chromatography/tandem spetrometry (Quintana and Reemtsma, 2007). To simplify Japan's recommended method of EDTA determination by using gas chromatography-mass spectrometry, we focused on the pretreatment of EDTA by using solid-phase extraction in the present study. In comparison with evaporation using rotary evaporator, solid-phase extraction is simple, rapid, and efficient.

MATERIALS AND METHODS

Chemicals

Ethylenediaminetetraacetic acid, disodium salt, dehydrate and trans-1, 2-cyclohexanediaminetetraacetic acid monohydrate (CyDTA) were obtained from Dojindo (Kumamoto, Japan) and Strem Chemicals, Inc. (Newburyport, MA, USA), respectively. Boron trifluoride methanol complex methanol solution, formic acid, potassium dihydrogenphosphate, sodium sulfate, sodium hydroxide, L(+)-ascorbic acid, methanol and dichloromethane were purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan). All chemicals and solutions were of analytical grade. Milli-Q water was used in all experiments.

Gas chromatography/mass spectrometry analysis

Gas chromatography was carried out by using HP6890 series gas chromatography system (Hewlett Packard, Wilmington, DE, USA) with an HP6890 series auto sampler and split/splitless injector. The analytical column was a DB-5 fused-silica capillary column, 30 m × 0.25 mm i.d., 0.25 μm film thickness (J & W Scientific, Folsom, CA, USA). The temperature program for the column oven was 70°C as initial temperature for 2 min; ramped at 15°C/min to 300°C then held at 300°C for 3 min. The carrier gas (helium) flow rate was set at 1.2 mL/min.

Mass spectrometry was carried out using a 5973 Mass Selective Detector (Hewlett Packard, Wilmington, DE, USA) in electron-ionization mode with an ionization voltage of 70 eV and ion source temperature of 230°C. The instrument was operated in selected-ion monitoring (SIM) mode. The monitor ion of EDTA and CyDTA were *m/z* of 174 (for identification : *m/z* = 289, 348) and 402, respectively. CyDTA was used as an internal standard.

Sample collection

River water samples used in this study were collected from six rivers located in the Shikoku region (Kochi and Tokushima prefectures), Kansai region (Hyogo and Kyoto prefectures), and Kanto region (Kanagawa Prefecture and Tokyo Metropolis) (Fig. 1). River water sampling was conducted in January (for Shikoku region and Hyogo Prefecture) and April (Kyoto Prefecture and Kanto region) 2010. River water samples were collected in 300 mL glass bottles and stored in the dark at 4°C until analysis.

Standard and sample preparation

A standard stock solution of EDTA was prepared by dissolving 0.127 g of ethylenediaminetetraacetic acid, disodium salt, dehydrate in 1 L Milli-Q water. On the

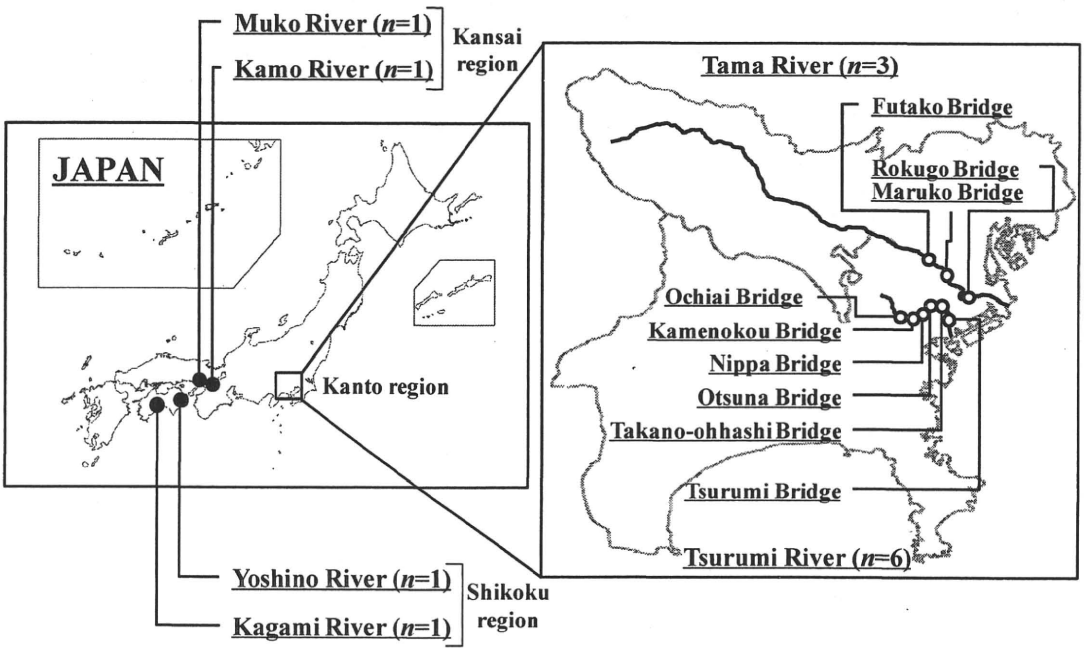

Fig. 1 - River water sampling locations

other hand, a standard stock solution of CyDTA was prepared by dissolving 0.01 g of trans-1, 2-cyclohexanediaminetetraacetic in 100 mL of 1 M sodium hydroxide.

Extraction of EDTA from water samples was performed according to the method of Knepper *et al.* (2005) with modifications. Water samples (100 mL each) were adjusted to pH 3 by 16 M formic acid and filtered with glass fiber filter (0.7 μm, Millipore, Billerica, MA, USA). Bond Elut Jr. –SAX (500 mg, Varian, Inc., Palo Alto, CA, USA) cartridges were conditioned with 3 mL methanol and 3 mL of Milli-Q water, respectively. Extraction of water samples was carried out at a flow rate of 10mL/min. After extraction, cartridges were rinsed with 3mL of Milli-Q water and eluted into stoppered glass test tubes with 3 mL of 16 M formic acid. The eluates combined with internal standard (CyDTA) were concentrated in a nitrogen stream at 80°C to complete dryness. After exsiccation, 1 mL of boron trifluoride-methanol-complex solution was added to the glass test tubes. Derivatization was carried out by 1 h heat treatment at 80°C using a water bath. After derivatization, 3 mL of 1 M phosphate buffer (pH 7) and 1mL of dichloromethane were added to the test tubes and rigorously shaken. Thereafter, test tubes were centrifuged for 5 min at 900 *g*. After centrifugation, the layer of dichloromethane was collected in a glass tube and dehydrated by sodium sulfate. The dehydrated dichloromethane solution was used for analysis. The limit of quantification (LOQ) was determined by analyzing the lowest level standard at least 5 times. The LOQ was calculated as 10-fold the standard deviation of these determinations. The LOQ value was 0.1 μg/L in sample water.

RESULTS AND DISCUSSION

Recovery experiments

To evaluate the efficiency, solid-phase extraction was performed as described below.

The EDTA standard solution was added to 100 mL Milli-Q water and tap water at concentrations of 0.1 mg/L (1/5 of EDTA standard value in drinking water) and 0.01 mg/L (1/50 of EDTA standard value in drinking water) and subsequent extraction and derivatization were carried out as described previously. Tap water samples were dechlorinated by L(+)-ascorbic acid before use. Control samples for recovery test by using Milli-Q water were prepared by adding the same amount of EDTA standard solutions to 3 mL Milli-Q water. In the case of using tap water for the recovery test, control samples were prepared by adding the same amount of EDTA standard solution to the eluate from tap water extraction. All controls, samples, and blanks were determined in triplicate. Recovery percentages of EDTA from Milli-Q and tap water samples are shown in Table 1. In the case of Milli-Q water samples, excellent recovery percentages at each concentration were obtained, and the values were 100.5% (concentration: 0.01 mg/L) and 100.2% (concentration: 0.1 mg/L). Moreover, the relative standard deviation (RSD) of the ratio of EDTA to CyDTA in each sample was within 5% (ranging from 0.3 to 4.2%) and the variability among samples was small. No influence of matrix from the SPE cartridge was observed in blank samples.

In order to apply the proposed method to actual tap water samples, a recovery test was performed using tap water (Table 1). Satisfactory results were obtained from recovery tests using tap water samples as well as those of Milli-Q water. Variability between samples was small and the pretreatment process of our method was simple and took a relatively short time compared with the existing Japanese Standard Methods for the Examination of Water. We therefore suggest that the SPE-derivatization-GC/MS method should be considered for the Japanese Standard Methods for the Examination of Water as an EDTA analytical method. The next stage to add this new SPE-derivatization-GC/MS method to the Japanese Standard Methods for the Examintion of Water would be to perform an inter-laboratory validation study of the proposed method.

Determination of EDTA in river water samples

For the application of this analytical method to environmental water samples, concentrations of EDTA in river water samples from urban and rural areas of Japan were investigated using SPE-derivatization-GC/MS. River water samples were taken from three regions of Japan (Fig 1). As shown in Fig 2, EDTA was detected in ten of thirteen river water samples. Although EDTA was not detected from river water samples of Kagami, Yoshino, and Kamo rivers (concentration: < 0.1 μg/L), EDTA was detected at comparatively high concentration in other river water samples. The median concentration of EDTA in river water samples was 115 μg/L and the concentrations detected ranged from 18.8 to 443 μg/L.

In the Kanto region, the highest concentration of EDTA (443 μg/L) was observed in a

Table 1 – Recovery of EDTA from Milli-Q water and tap water samples

Analyte	Vehicle	Concentration (mg/L)	Recovery of triplicate samples (%) A	B	C	Mean	SD
EDTA	Milli-Q water	0.01	100.1	100.9	100.6	100.5	0.4
	Milli-Q water	0.1	100.0	99.8	100.8	100.2	0.5
	Tap water	0.01	102.0	98.7	99.8	100.1	1.7
	Tap water	0.1	98.3	98.9	97.2	98.1	0.9

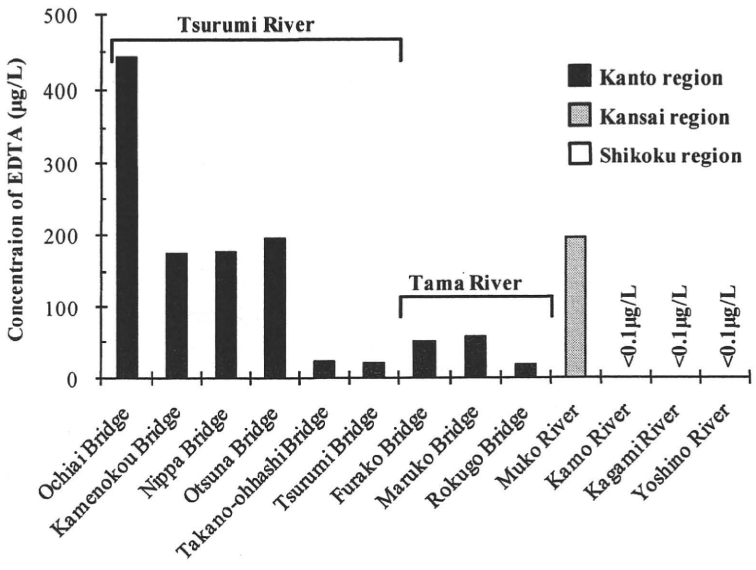

Fig.2 - Concentration of EDTA in river water samples from three regions of Japan

river water sample collected at Ochiai Bridge of Tsurumi River. It is generally considered that effluent from sewage treatment plants (STP) is one of the major sources of EDTA (Kari and Giger, 1996). This sampling site is located at about 150 m downstream from the effluent output of an STP and the contribution of effluent to the EDTA concentration is high. In Tsurumi River, there are three STPs near the sampling sites. Two STPs are located upstream of Ochiai Bridge and between Kamenokou Bridge and Nippa Bridge, respectively. Moreover an STP is located at Yagami River (tributary of Tsurumi River) between Otsuna Bridge and Takano-ohhashi Bridge. The river water sample taken from Nippa Bridge contained high levels of EDTA. The EDTA concentration of the river water sample taken from Takano-ohhashi bridge was lower than those of other river water samples collected downstream of STPs. Because the STP is located on a tributary of Tsurumi River, the EDTA concentration might be affected by dilution with the influent of Yagami River at this sampling site. The low EDTA concentration in the river water sample from Tsurumi Bridge (downstream of Tsurumi River) might also be caused by dilution. EDTA concentrations of Tama River samples ranged from 18.8 to 56.8 μg/L and the values were comparatively lower than those from Tsurumi River. These sampling sites were located at lower-middle and lower portions of Tama River while the STPs are located at the upper-middle portion of Tama River. Therefore, it was concluded that concentrations of EDTA decreased going downstream due to dilution. In Kansai region, EDTA was only detected in the river water sample of Muko River and the value (196 μg/L) was comparable to that of Tsurumi River. There is an STP in the upper part of Muko River and EDTA may originate from that source. However, because there is no STP upstream of the sampling site of Kamo River, EDTA was not detected in Kamo River sample. On the other hand, in Shikoku region, EDTA was not observed in the river water samples. The concentration of EDTA might be low due to these samples being collected in estuarine regions. In further studies, it will be necessary to survey the differences in EDTA contamination levels between urban and rural areas.