Emerging Disinfection By-Products of Toxicological Interest: Results of a Nationwide Occurrence Study

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Year of Water: Thirty Years of Progress Through Partnering

EnvironmentalIssue

TheSafeDrinkingWaterActandAmendmentsrequiresthatEPAaddress disinfectionby-products(DBPs)indrinkingwater.DBPsareformedwhena disinfectant(suchaschlorine)reactswithorganicmatterand/orbromide naturallypresentinsourcewaters.Drinkingwaterdisinfectionby-products (DBPs)areofconcernbecauseepidemiologicstudiesindicatethatsomemay beassociatedwithcancerandadversereproductive/developmentaleffectsin humanpopulations,andotherstudieshaveshownthatcertainDBPscause cancerandadversereproductive/developmentaleffectsinlaboratoryanimals. AfewDBPsareregulated;however,mostDBPshavenotbeentestedfor adversehealtheffectsduetohighcostsinvolved. Inordertoprioritizenew DBPsforhealtheffectstesting,weinitiatedaNationwideOccurrenceStudyto quantify'highpriority'DBPsthatwereselectedfromanextensiveprioritization effortofallDBPsthathadeverbeenreported. DBPswereprioritized accordingtopredictedadversehealtheffects(cancer)byamultidisciplinary groupofexperts,includingtoxicologists,structure-activityspecialists,and chemists (*1*). ThefateandtransportoftheseDBPsinthedistributionsystem wasalsostudied,andnewDBPswereidentified. Scientistsfromthe UniversityofNorthCarolinaandtheMetropolitanWaterDistrictofSouthern Californiacollaboratedwith NERLscientistsonthiseffort.

Table1.HighpriorityDBPsincludedinNationwideDBPOccurrenceStudy

MXandMX-Analogs:
3-Chloro-4-(dichloromethyl)-5-hydroxy-2(5H)-furanone(MX)
3-Chloro-4-(dichloromethyl)-2-(5H)-furanone(red-MX)
(E)-2-Chloro-3-(dichloromethyl)-butenedioicacid(ox-MX)
(E)-2-Chloro-3-(dichloromethyl)-4-oxobutenoicacid(EMX)
2,3-Dichloro-4-oxobutenoicacid(Mucochloricacid)
3-Chloro-4-(bromochloromethyl)-5-hydroxy-2(5H)-furanone(BMX-1)
3-Chloro-4-(dibromomethyl)-5-hydroxy-2(5H)-furanone(BMX-2)
3-Bromo-4-(dibromomethyl)-5-hydroxy-2(5H)-furanone(BMX-3)
(E)-2-Chloro-3-(bromochloromethyl)-4-oxobutenoicacid(BEMX-1)[f]
(E)-2-Chloro-3-(dibromomethyl)-4-oxobutenoicacid(BEMX-2)[f]
(E)-2-Bromo-3-(dibromomethyl)-4-oxobutenoicacid(BEMX-3)[f]

Haloacids:
3,3-Dichloropropenoicacid

Halomethanes:
Chloromethane
Bromomethane(methylbromide)[a]
Dibromomethane
Bromochloromethane
Bromochloroiodomethane
Dichloroiodomethane
Dibromoiodomethane[a]
Chlorodiiodomethane[a]
Bromodiiodomethane[a]
Iodoform[a]
Chlorotribromomethane
Carbontetrachloride

Halonitromethanes:
Bromonitromethane
Chloronitromethane[a]
Dibromonitromethane
Dichloronitromethane[a]
Bromochloronitromethane[a]
Bromodichloronitromethane[a]
Dibromochloronitromethane[a]
Tribromonitromethane(bromopicrin)[a]

Haloacetonitriles:
Bromoacetonitrile
Chloroacetonitrile
Tribromoacetonitrile
Bromodichloroacetonitrile
Dibromochloroacetonitrile

Haloketones:
Chloropropanone
1,3-Dichloropropanone
1,1-Dibromopropanone1,1,3-Trichloropropanone
1-Bromo-1,1-dichloropropanone
1,1,1,3-Tetrachloropropanone
1,1,3,3-Tetrachloropropanone
1,1,3,3-Tetrabromopropanone[a]
1,1,1,3,3-Pentachloropropanone
Hexachloropropanone

Haloaldehydes:
Chloroacetaldehyde
Dichloroacetaldehyde
Bromochloroacetaldehyde[b]
Tribromoacetaldehyde[b]

Haloacetates:
Bromochloromethylacetate

Haloamides:
Monochloroacetamide[a]
Monobromoacetamide[a]
Dichloroacetamide
Dibromoacetamide[a]
Trichloroacetamide[a]

Non-HalogenatedAldehydesand Ketones:
2-Hexenal
5-Keto-1-hexanal[c]
Cyanoformaldehyde
Methylethylketone(2-butanone)[c]
6-Hydroxy-2-hexanone[c]
Dimethylglyoxal(2,3-butanedione)

Volatileorganiccompounds(VOCs) andMiscellaneousDBPs:
1,1,1,2-Tetrabromo-2-chloroethane
1,1,2,2-Tetrabromo-2-chloroethane[a]
Methyl-tert-butylether[d]
Benzylchloride

[a]NotaDBP,butincludedbecauseit isanimportantsourcewater contaminant.

[b]DBPnotoriginallyprioritized (identifiedindrinkingwaterafter initialprioritization),butincludeddue tosimilaritytootherpriority compounds.

[c]DBPnotgivenahighpriority,but includedforcompletenesssaketo providemorerepresentationto ozoneDBPsforoccurrence.

ScientificApproach

Drinkingwaterswerechosenacrosstheunitedstatesinlocationstoprovide waterswithlowandhighbromide,differentpHconditions,anddifferentorganic matterlevels.RegulatedandInformationCollectionRuleDBPswerealso measuredforcomparisonpurposes. Sampleswerecollectedquarterlyfrom the12treatmentplantsstudied. Analyticalmethodsdevelopedforquantifying thehighpriorityDBPsindrinkingwaterincluded,andmassspectrometry methodswereusedtoidentifynewDBPs. Analyticaltechniquesthatwere usedtomeasurethesehighpriorityDBPsincludemethylationwithgas chromatography(GC)-electroncapturedetection(ECD)fortheMXanalogs andhaloacids,pentafluorobenzylhydroxylamine(PFBHA)derivatizationwith GC-ECDforcarbonylcompounds,liquid-liquidextraction-GC-ECDfor haloamidesandhaloacetates;andliquid-liquid-extraction-GC-ECD,solidphase extraction(SPE)-GC/massspectrometry(MS),andpurge-and-trap-GC/MSfor halonitromethanes,iodo-THMs,otherhalomethanes,haloaldehydes, haloketones,andhaloacetonitriles. GCwithlowandhighresolutionMSwas usedtoidentifynewDBPs.

SamplingSurvey:

- 12plantssampledquarterly
- 2plants-samewatershed-differenttreatment/disinfection
- PlantssampledinEPARegions3,4,5,6,7,and9

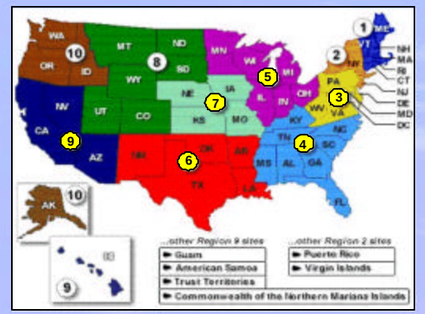
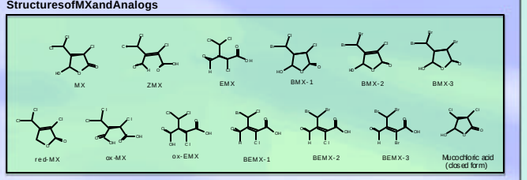


Table2.DrinkingWaterUtilitiesSampled

Utility (EPA Region)	Disinfection Used
Plant 1 (EPA Region 9)	Ozone-chlorine-chloramines
Plant 2 (EPA Region 9)	Chlorine-chloramines
Plant 3 (EPA Region 6)	Chlorine dioxide-Chloramines
Plant 11 (EPA Region 6)	Chlorine dioxide-chlorine-chloramines
Plant 8 (EPA Region 4)	Chlorine-chloramines
Plant 7 (EPA Region 4)	Chloramines-ozone
Plant 6 (EPA Region 4)	Chlorine dioxide-chlorine-chloramines
Plant 5 (EPA Region 4)	Ozone-chlorine
Plant 9 (EPA Region 3)	Chlorine-chloramines
Plant 4 (EPA Region 3)	Chlorine
Plant 10 (EPA Region 5)	Chlorine-chloramines
Plant 12 (EPA Region 7)	Chlorine-chloramines

StructuresofMXandAnalogs



Results

Halonitromethanes*
- Individualhalonitromethanes0.1to3ppb
- Dichloro-,bromochloro-,bromodichloro-,and dibromochloronitromethanemostprevalent formsobserved
- Insomecases,pre-ozonationincreased formationofbrominatedtrihalonitromethanes (includingtribromonitromethane(bromopicrin))

*Inmammaliancellassays,bromonitromethanes havebeenshowntobeatleastanorderof magnitudemoregenotoxictomammaliancellsthan MXandhavegenotoxicitiesgreaterthanallofthe haloaceticacidDBPsregulatedintheUnitedStates, exceptformonobromoaceticacid(*3*).

Halofuranones(MXanalogs)
- Widelyobserved
- Often>100ng/L
- Max310ng/L(plantwithhighTOC,chlorine dioxide-chlorine-chloraminetreatment;not detecteduntilafterchlorine/chloramine treatment)
- BMXsidentified(170&200ng/LforBMX-1 andBEMX-3atonelocationwithhigh bromide)

Haloacetaldehydes
- Haloacetaldehydes3rdlargestfraction(bywt) ofhalo-DBPs
- Mostlyduetodichloroacetaldehyde(inaddition tochloralhydrate)
- Dichloroacetaldehydedetectedatlowppbto 16ppb;highestataplantusingchloramines& ozone

Newlodo-Acids*
- Iodoaceticacid
- Iodobromoaceticacid
- 3-Iodo-3-bromopropenoicacid(2isomers)
- 2-Iodo-3-methylbutenedioicacid

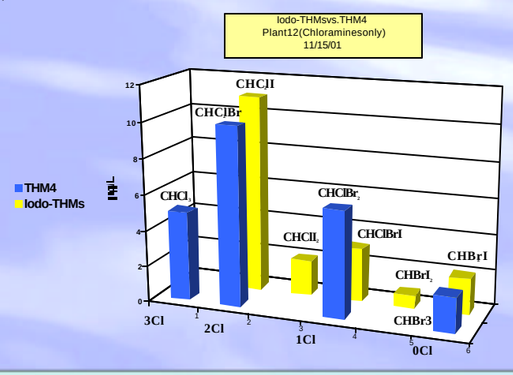
*Intoxicologicstudiesofiodoaceticacid(mammalian cellandinvivo developmentalassays),iodoacetic acidcauseddevelopmentaleffectsinmouseembryos (neuraltubeclosures)atlowMlevels(),3odoacetic acidwasalsoapproximately3-foldmoregenotoxic andcytotoxicthanbromoaceticacidtomammalian cells(*4*).

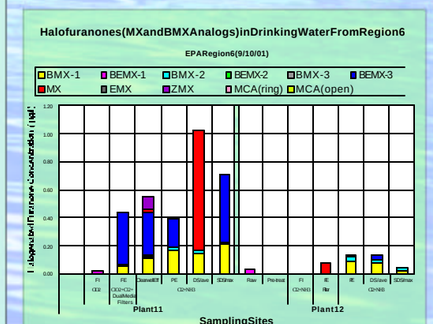
Iodo-Trihalomethanes(THMs)
- Individualiodo-THMs0.2to15ppb
- Totaliodo-THMs(whendetected):2-81%of THM4(sumof4regulatedTHMs)
- Highestataplantusingchloramines(andno pre-chlorine)
- Dichloroiodomethanethemostcommon

Haloacids
- 3,3-Dichloropropenoicacidhighpriority DBP measured
- Foundindrinkingwaterfrommostplants sampled
- 0.1to5.5ppb
- Therefore,higherchainhalo-acids(notjust haloaceticacids)likelysignificantindrinking water

Haloamides
- Newclassnotpreviouslymeasured
- Foundinmostplantssampled
- Individualhaloamidesrangedfrom0.1 to9.4 ppb
- Levelssimilartoothercommonlymeasured DBPs

DistributionSystem(DS)&SimulatedDS Tests
- Chloramines: MostDBPsstable (exceptfor highpHwaters)
- Freechlorine: THMs,haloaceticacids(HAAs) increase
- Haloacetonitriles,halonitromethanes, haloaceteldehydes: Typicallystable (noneof thesystemswithfreechlorinewereathighpH levels)
- Haloketones: Somedegraded
- BMXs: Mostlystable
- MXs: Sometimesstable,sometimesdegraded –butnevercompletelydegraded





ImportantFindings

- ManyofthehighpriorityDBPsfoundindrinkingwaters acrosstheU.S.
- MXlevelsexceededpreviouslevelsinlimitedstudies conductedtodate(300-400ng/Lfound);BMXsreached 100-200ng/L
- Althoughtheuseofalternativedisinfectantsminimizedthe formation ofTHM4,certainotherDBPsformedat significantconcentrations:
  - Iodo-THMshighestataplantusingchloramines
  - Bromotrihalonitromethaneshighestataplantusingpre-ozonation
  - Dichloroacetaldehydehighestatplantsusing chloramines&ozone
  - MXandBMXshighestatplantsusingchlorinedioxide (followedbychlorine-chloramines)thattreatedwaters highinNOMandbromide;chlorinedioxidedidnot removeMXprecursors
- Thepresenceofbromideresultedinashiftinspeciationfor THMs,HAAs,andotherclassesofDBPs
- Iodo-acidsidentifiedforthefirsttime(alsonewbromo-acids)

ImpactofthisStudy

Thisresearchexpandsourknowledgeontheoccurrenceof DBPsbeyondthosethatarecurrentlyregulated,willhelpto prioritizefutureDBPhealtheffectsresearch,andwillallow EPA'sOfficeofWatertomakeimproveddecisionsregarding thesafetyofdrinkingwaterandtoultimatelyminimizeany thatarefoundtobehazardous.

References

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Partnering to Protect Human Health and the Environment