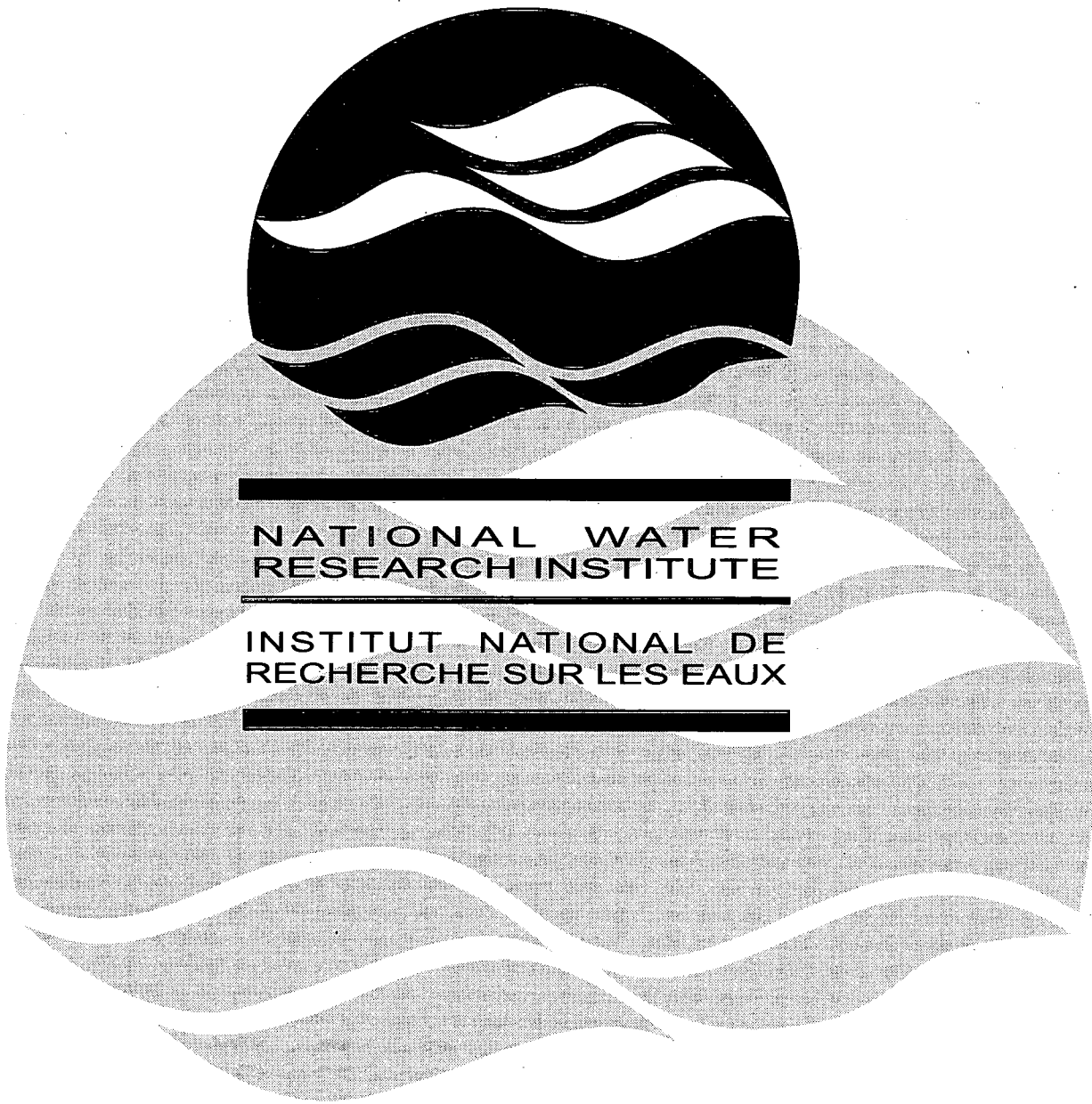


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**NORTHERN CONTAMINANTS INTERLABORATORY
QUALITY ASSURANCE PROGRAM FOR 1998/99**

Y.D. Stokker

NWRI Contribution No. 99-303

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**NORTHERN CONTAMINANTS INTERLABORATORY
QUALITY ASSURANCE PROGRAM FOR 1998/99**

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MANAGEMENT PERSPECTIVE

This report describes the quality assurance (QA) activities conducted by Environment Canada during 1998/99 in support of the Northern Contaminants Program (NCP). Because it was the first year for Phase II of the NCP (1998-2003), efforts were focused on updating information on the organizations contributing scientific data to the NCP-funded research projects, on identifying the relevant analytes and matrices for the QA program, and on evaluating the suitability of several external intercomparison programs for the NCP data quality needs. With this information, recommendations are made for an appropriately designed, ongoing QA program for Phase II of the NCP.

The purpose of the NCP Interlaboratory QA Program, coordinated by Environment Canada, is to provide information to the NCP science managers on the quality, reliability and comparability of measurement results produced by laboratories generating data for NCP-funded research projects. The main activities are the intercomparison exercises, focusing on contaminants of concern to Canada's northerners. These studies also provide a means for continual improvement in the measurement process for the laboratories involved. The NCP QA program therefore assists NCP science managers and northerners to make informed decisions on the sources of contaminants and their effects on the Arctic environment and on human health, while ensuring that the NCP's contributions to international agreements and controls to protect the health of the Arctic ecosystem and northerners are based on scientifically sound data.

PERSPECTIVE DE LA DIRECTION

Ce rapport décrit les activités d'assurance de la qualité (AQ) menées par Environnement Canada en 1998-1999 à l'appui du Programme de lutte contre les contaminants dans le Nord (PLCN). Étant donné qu'il s'agissait de la première année de la Phase II du PLCN (1998-2003), les efforts ont porté surtout sur la mise à jour des renseignements sur les organisations qui contribuent des données scientifiques aux projets de recherche financés dans le cadre du PLCN, sur l'identification des analytes et des matrices qui devraient être visés par le programme d'AQ et sur l'évaluation de plusieurs programmes interlaboratoires externes pour déterminer si la qualité des données qu'ils fournissent satisfait aux besoins du PLNC. Cette information permet de faire des recommandations en vue de la mise sur pied d'un programme continu et bien conçu d'AQ pour la Phase II du PLCN.

Le Programme interlaboratoires d'assurance de la qualité du PLNC, qui est coordonné par Environnement Canada, a été créé pour fournir de l'information aux gestionnaires scientifiques du PLNC sur la qualité, la fiabilité et la comparabilité des résultats de mesure obtenus par les laboratoires générant des données pour les projets de recherche financés par le PLNC. Les principales activités sont les exercices de comparaison portant sur les contaminants qui présentant un intérêt pour les populations du Nord du Canada. Ces études permettent également l'amélioration continue des processus de mesure utilisés par les laboratoires participants. Le programme d'AQ du PLNC aide donc les gestionnaires scientifiques du PLNC et les populations nordiques à prendre des décisions éclairées concernant les sources des contaminants et leurs effets sur l'environnement arctique et sur la population humaine, tout en faisant en sorte que les contributions du PLCN aux ententes et à la surveillance internationale visant à protéger la santé de l'écosystème arctique et des populations nordiques soient fondées sur des données scientifiques valables.

ABSTRACT

This report summarizes the quality assurance activities supporting the Northern Contaminants Program (NCP) during 1998/99. The main thrust of the year's efforts was directed at updating information on the NCP measurement laboratories, and at identifying the matrices and contaminants under study in the NCP-funded research projects of Phase II of the NCP. The results of two surveys (one detailing the analytical capabilities of the NCP-funded laboratories and the other assessing the suitability of external interlaboratory QA programs for the NCP), are summarized in this report. Based on these two surveys, and the aim of NCP Phase II to focus on traditionally-harvested foods, several recommendations are made for the future direction of the NCP QA Program. This report also summarizes the development of a list of 'mandatory' PCB congeners for NCP research, and describes the successful results for an interlaboratory assessment on the analysis of trace metals in sediment samples.

RÉSUMÉ

Ce rapport résume les activités d'assurance de la qualité menées en 1998-1999 à l'appui du Programme de lutte contre les contaminants dans le Nord (PLCN). Au cours de cette année, les efforts ont surtout porté sur la mise à jour de l'information sur les laboratoires de mesure du PLCN et sur la détermination des matrices et des contaminants étudiés dans le cadre des projets de recherche financés au cours de la Phase II du PLNC. Les résultats de deux enquêtes (l'une détaillant les capacités analytiques des laboratoires financés par le PLNC et l'autre évaluant l'utilité des programmes interlaboratoires externes d'AQ pour le PLCN) sont résumés dans ce rapport. En se fondant sur les recommandations de ces deux enquêtes et sur l'objectif de la Phase II du PLCN de mettre l'accent sur les aliments traditionnels, on a fait plusieurs recommandations concernant l'orientation future du programme d'AQ du PLCN. Le rapport donne également un aperçu du processus d'élaboration d'une liste de congénères des PCB devant «obligatoirement» être étudiés par le PLCN et décrit les résultats attendus d'une évaluation interlaboratoires de l'analyse des métaux-traces dans des échantillons de sédiments.

**NORTHERN CONTAMINANTS INTERLABORATORY QUALITY ASSURANCE
PROGRAM for 1998/99**

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Project Team: Ed Kaminski, NWRI; Glynn Gomes, Gomes Consulting Enterprises; Johan van Hoewelingen, Hogeschool van Utrecht, The Netherlands; members of the NCP Quality Assurance Sub-committee; all measurement laboratories in the Northern Contaminants Program.

OBJECTIVES:

Short-term:

1. Conduct intercomparison exercises on various contaminants of concern, such as persistent organic pollutants, radionuclides and heavy metals, in order to
 - a) ensure laboratories conducting measurements for the NCP are producing reliable data with acceptable levels of precision and accuracy;
 - b) ensure comparability between laboratories; and
 - c) provide a diagnostic tool for the measurement laboratories of the NCP to apply corrective measures, as needed.
2. Propose, coordinate and review participation by NCP measurement laboratories in external national and international interlaboratory comparison exercises where such participation would be considered to be more cost-effective and where it would add value to the NCP QA program.

Long-term:

1. Maintain up-to-date information on the analytical programs and capabilities of the laboratories and organizations that contribute measurement data to the NCP.
2. Design and conduct a program that delivers a series of appropriate interlaboratory comparison studies that will provide the NCP research project leaders, ongoing assurance of the quality, reliability, and comparability of measurement results produced by laboratories contributing data to their NCP research studies.
3. Conduct surveys, interlaboratory study assessments and external intercomparison reviews, to identify sources of measurement uncertainties and variation among analytical results in order to provide information on overall data quality and reliability to the science managers of the NCP.

DESCRIPTION

The Northern Contaminants Program (NCP), like all research and monitoring programs, requires an on-going quality assurance (QA) program that provides assurance to its managers of the quality, reliability and comparability of measurement results being generated for their research projects. At the same time, it should meet the diverse QA/QC needs of the researchers and analysts by providing them with appropriate diagnostic tools for their analyses and offering guidance and support toward corrective measures, if needed. This interlaboratory QA program of the NCP aims to identify sources of measurement uncertainties and variation of analytical results in order to provide information on data quality to the management of the NCP.

This past year saw a shift in focus within the NCP from the Phase I interest in pathways, trends and controls of contaminants in the Arctic environment to the Phase II interest in human health and safety issues associated with

contaminants in traditionally harvested foods for Northern people. As a result, the initial 1998/99 activities of the QA program focused on identifying who the measurement laboratories are that contribute analytical data to the NCP, and specifically where their interests and capabilities lie.

NCP-funded research and monitoring studies involve the analysis of a wide variety of different contaminants at trace and ultra-trace levels in various matrices including air, snow, water, sediments, plants, fish, mammals and human tissue samples. It is such a diverse program that the question of comparability of data among the different measurement laboratories and between individual projects becomes difficult to assess. Ideally, a carefully designed QA program would ensure the reliability and comparability of analytical results for all target contaminants in each matrix and species, as well as among the individual laboratories contributing the measurement data. Unfortunately, such a broad scope of activities would be too costly. Consequently, a survey of national and international external interlaboratory study providers was undertaken to determine where participation in external intercomparisons would be more cost-effective to the NCP QA program while still providing adequate assurance of NCP data quality.

Because the NCP-funded projects target contaminants in many different matrices and species, there is no single matrix sample that would be suitable for evaluating all participating laboratories. One way to accommodate such diversity is to include check samples prepared in solution form. Intercomparison study participants should then use their own routine methodology and analytical calibration standards. This interlaboratory QA program has been designed to incorporate a variety of natural materials in future interlaboratory studies, in order to achieve an increasing progression of complexity in the test samples. In addition, a small repository of surplus samples with known target parameter concentrations will be made available to NCP laboratories that experience

difficulties with the study samples and therefore require additional test material to evaluate the success of their corrective actions.

The submitted laboratory data for both the standard solutions and matrix test samples are evaluated for accuracy and comparability by Z-scores and by comparison to the target concentrations, for precision on replicate analyses (or by percent difference on blind duplicate samples), and for bias by a modified Youden ranking procedure. The data assessment is then used as a diagnostic tool for the participants to apply corrective action, if needed. Finally, the complete study report provides a snapshot of data quality to the science managers of the NCP along with an overview of the capabilities and comparability of the NCP laboratories conducting these measurements.

ACTIVITIES IN 1998/99

The QA program of Phase II of the NCP began with a survey¹ of the project leaders and the laboratories conducting analyses for the NCP (i.e. using NCP funds). The purpose of the survey was to identify the laboratories conducting NCP-funded measurements and compile information on their analytical capabilities as well as to determine the relevant matrices, analytes and contaminant levels for the quality assurance program. The resultant inventory of laboratories and measurement analyses, was then used to determine current QA needs and to prioritize future NCP QA activities.

A second (concurrent) survey² of external national and international QA programs was conducted to identify external intercomparison studies that would complement those run in the NCP QA program. This survey assessed the suitability of each external QA program in terms of parameters and concentration levels, test sample matrix, cost, and timing and frequency of the studies. In making recommendations on the use of these external programs to support the

NCP's QA needs, additional factors, such as the number of NCP-funded laboratories for which these external intercomparisons would be appropriate, were also considered.

At the request of the QA Technical Sub-committee, efforts were also directed this year, at developing a list of PCB congeners that could be made mandatory for all NCP-funded PCB analyses. A small database was compiled for PCB congeners reported in the literature for various marine or Arctic matrices. The selection of congeners was based on their toxicity, frequency of occurrence and concentration levels relative to the (reported) Total PCB levels. Comparisons were made to existing PCB congener lists in other external research and QA programs. The proposed NCP list of PCB congeners will be forwarded to the measurement laboratories for comments and to the QA Technical Sub-committee for their review.

The first intercomparison study for Phase II of the NCP (Interlaboratory Study NCP-II-1) was conducted on the analysis for trace metals in sediment. While the study focused on the key elements of mercury, selenium and cadmium, the participants were only obliged to analyze and report on the analytes of interest to their respective projects. Eight laboratories provided results, and most participants analyzed for at least ten of the sixteen target parameters.

RESULTS

Survey 1. The information for the first survey report¹ was gathered via a written questionnaire that sought information on contact persons, analytical capabilities of the laboratories, analytes, concentration levels and matrices, methodologies and instrumentation, the use of certified reference materials (CRMs), and participation in any external interlaboratory studies. The survey questionnaire

was sent to more than twenty project leaders who were identified as receiving NCP funding.

For 1998/99, the number of NCP measurement laboratories conducting analyses on the various sample types were as follows:

various biotic samples	19
fish.....	13
water.....	18
sediment/soil.....	13
human food stuffs.....	4
animal feed	2
snow	4
urine.....	6
blood.....	6
mining products and effluents.....	4

Thus, biotic samples of one form or another were the most commonly analyzed matrix material, with water and sediment samples also being quite common among the laboratories surveyed.

The survey also identified the number of laboratories conducting analyses for the different contaminants of interest to the NCP as follows:

trace metals	12
mercury.....	13
methylmercury	2
organotins	2
radionuclides.....	6
nutrients (in water)	4
organochlorine pesticides (OCs) and PCBs	16
toxaphene.....	8
dioxins and furans.....	8
polynuclear aromatic hydrocarbons (PAHs)	4
brominated diphenyl ethers (BPDEs).....	1

Clearly, there are sufficient NCP laboratories to justify conducting a series of intercomparison studies for OCs/PCBs, toxaphene, dioxins and trace metals. However, for nutrients in water, PAHs, organotins, and methylmercury, where fewer than five NCP laboratories conduct such analyses, a closer scrutiny of available external options would help to determine the most effective means of assuring the quality and intercomparability of these NCP measurements.

Survey 2. The questionnaire for the second survey sought to identify available external intercomparison studies that would complement the NCP QA program by bridging gaps, particularly for those parameters listed above, where fewer than 5 NCP laboratories would be involved.

The survey² revealed that participation in the following external QA programs would enable the NCP QA program to assess data quality for a much broader range of analytes and matrices than could be covered by the NCP intercomparisons alone:

- (a) QUASIMEME (Quality Assurance of Information for Marine Environmental Monitoring in Europe, FRS Marine Laboratory, Aberdeen, Scotland), particularly for its toxaphene and organotin development exercises,
- (b) CAEAL (Canadian Association for Environmental Analytical Laboratories, Ottawa, Canada) and NWRI (National Water Research Institute, Burlington, Ontario, Canada) for nutrients in water,
- (c) the NOAA (National Oceanic and Atmospheric Administration, Silver Spring, Maryland, USA) program for trace metals in sediment and biota run by the National Research Council of Canada, Ottawa
- (d) the IAEA (International Atomic Energy Agency, Vienna, Austria) intercomparison exercises for radionuclides, and when available, for organotins and methylmercury,
- (e) and the blood and urine intercomparison studies conducted by CTQ (Centre de Toxicologie du Quebec) and the Great Lakes Research Centre (Michigan, USA) for metals and PCBs, respectively.

Development of a list of 'mandatory' PCB congeners. A literature review was conducted on the PCB congener levels reported for samples from marine and Arctic origins. Tables of data have been compiled for each of the following matrices: water, air/snow/rain, vegetation, sediment, fish, mussels, mammalian and bird tissues, blood (human and seal), and other human tissue samples. When potential toxicity, environmental prevalence, and relative abundance in animal tissues are used as criteria, the number of environmentally threatening PCB congeners reduces to about thirty-six. Twenty-five of these account for 50-75% of total PCBs in tissue samples of fish, invertebrates, birds and mammals.

The proposed list has been compared to the IADN (Integrated Atmospheric Deposition Network) list, the List of POPs recommended for AMAP (Arctic Monitoring and Assessment Programme), the Quebec Ministry of Environment congener mix, and the target congeners for external intercomparison studies offered by QUASIMEME, IAEA and NOAA.

Interlaboratory Study NCP-II-1. Trace metals in sediment. Eight laboratories provided trace metal results on the four sediment check samples. For most of the metals, the data were quite comparable, as demonstrated by coefficients of variation of less than 25%. The parameters that showed the least comparability were chromium, selenium and vanadium. The repeatability of analysis for each participant was quite good on the duplicate samples, with only one laboratory exceeding 10% difference between duplicates for more than one metal. All laboratories exhibited some bias for at least one of the target parameters. Z-scores for all key toxic metals were less than 2.

Overall, the results of the trace metal in sediment interlaboratory study³ were in good agreement with previous trace metal assessments conducted by the NWRI on sediment samples, and are in keeping with assessments reported by

QUASIMEME, IAEA and NOAA-NRC. A second intercomparison on trace metals in biota is currently being conducted.

DISCUSSION/CONCLUSIONS

Quality Assurance and quality control are essential elements of all research and monitoring programs. Ongoing interlaboratory comparison studies provide assurance on the quality of data being generated and on the comparability of measurement results between laboratories. Without this assurance of data quality and comparability, the value of measurement information upon which decisions are made will be lost. It is imperative that managers and decision makers of the NCP have a scientifically sound science base upon which to base their decisions.

The two surveys^{1,2} identified some parameter/matrix combinations for which the quality of data is already being competently addressed by other QA programs. Examples are the CAEAL and NWRI studies for trace metals (including mercury) and nutrients in water, and the IAEA intercomparisons for radionuclide measurements. In addition, several of the larger facilities include participation in pertinent interlaboratory studies as part of their own Quality Management System. However, it also was evident that many of the smaller NCP measurement laboratories are not participating in any pertinent external QA programs. Furthermore, the availability of external intercomparisons for less common contaminants of interest, such as organotins and methylmercury, are infrequent and may not address the matrix or concentration levels necessary.

The current recommendations for the NCP interlaboratory QA program are

- (a) to conduct interlaboratory studies for OCs/PCBs that specifically address parameters such as HCHs, chlordanes, and PCB congeners at appropriate levels in both biotic and abiotic samples,

- (b) to establish a series of intercomparison studies to monitor the quality of toxaphene data being generated, where external intercomparison studies are either not available or are not suitable to the work of the NCP laboratories,
- (c) to continue to address the data quality of trace metal analyses, including those for mercury, methylmercury and selenium, where feasible,
- (d) to make participation in an appropriate external Nutrients in Water QA program mandatory for the laboratories conducting such analyses,
- (e) to encourage participation by the radionuclide measurement facilities in the IAEA QA program, and
- (f) to address the comparability of measurements for analyses of organotins, dioxins and PAHs, as needed.

Thus, interlaboratory comparison exercises are, and will continue to be the main activities of this QA program. Other activities, such as a maintaining an inventory of laboratories and their capabilities, and a list of external sources of QA support such as intercomparisons and reference materials, are also important to achieve the goals of this program. The combination of these efforts will not only provide for an evaluation of data quality within the NCP, but will also provide a means for continual improvement in the measurement process for the laboratories involved.

EXPECTED COMPLETION DATE

The two surveys^{1,2} were completed in January 1998. As recommended by the QA Technical Sub-committee an update of the laboratory survey will be provided annually prior to their review of the proposal for the next fiscal year's QA program.

The preliminary data review for the trace metals in sediment study was provided to the participating laboratories in April 1999 and a report describing the full

assessment of trace metal capabilities and comparability will be provided by September 1999.³

The assessment of analytical comparability for other contaminants and matrices is an on-going process, with two additional intercomparisons being scheduled for 1999/2000. The test samples for Interlaboratory Study NCP-II-2 on trace metals and methylmercury in fish and marine mammal tissue were delivered to participants in July 1999; a final report will be provided to the participants by November 1999. Interlaboratory Study NCP-II-3 on the analysis of persistent organic pollutants in fish is being targeted for September through December 1999, after the proposed list of mandatory PCB congeners is reviewed by the QA Technical Sub-committee.

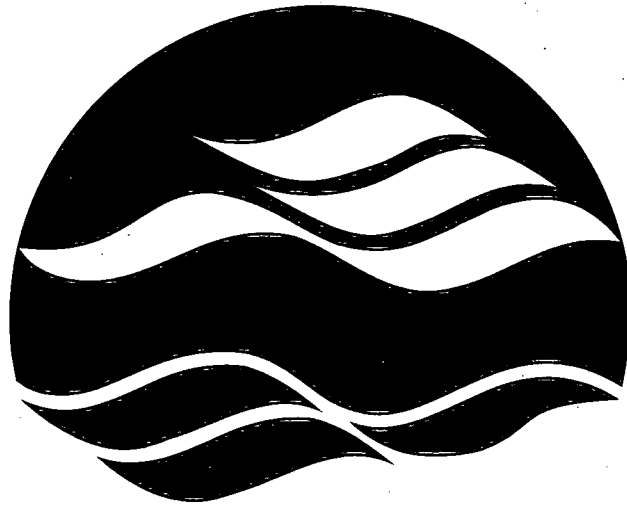
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